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Programa de Doctorat de Ciències Ambientals
Opció: Anàlisis del Medi Natural

LONG-RANGE ATMOSPHERIC TRANSPORT AND FATE OF PERSISTENT ORGANIC POLLUTANTS IN REMOTE MOUNTAIN AREAS

Barend L. van Drooge
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A l´últim bes del sol ponent, blanqueja
com un colom entre el fullatge verd;
perquè de lluny algun pastor no el veja,
de cortines de boira s´ha cobert.

Està enmig de l´estany com una estrella
florida enmig del cel de juliol,
nimfea colossal que s´esbadella
al bes de les escumes i del sol.

Per ses arrels lo lliguen a la vora,
com branques de coral esblanqueït,
quatre ponts de cristall del que atresora
la serra en ses entranyes de granit.

(fragment from El Canigó, Jacint Verdaguer (1885))

For Íngrid.

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Samenvatting

Persistente organische contaminanten (POP), zoals HCB, PCBs, DDTs, HCHs endosulfanen en PAKs, zijn wijd verspreid over het aardoppervlak. De meeste componenten zijn ooit gesynthetiseerd ten bate van de menselijke ontwikkeling, zonder in eerste instanite rekening te houden met de hun weerstand tegen biologische, chemische en fysieke degradatie, accumulatie in organisch material en toxiciteit.

In de gepresenteerde studie wordt de rol getoetst van de atmosfeer in de distributie van POP in afgelegen berggebieden, en ook het lot van deze componenten in bodem en sedimenten van hooggebergtemeertjes. De POP niveaus in de subtropische troposfeer van Tenerife en de Europese hooggebergten van de Centrale Pyreneeën en de Hoge Tatras zijn aan de lagere zijde van de waarden die elders gevonden worden. Op alle monsternamepunten zijn de meeste POP goed door de atmosfeer gemengd, wat duidt op het belang van atmosferisch transport over lange afstand. Naast actieve lucht monstername m.b.v. een HiVol-monsternameapparaat is er passieve monstername van lucht toegepast in de vorm van dennennaalden van de *Pinus uncinata* en half-doorlaatbare membranen (SPMDs) voor de studie van de ruimtelijke en tijdelijke distributie van organische chloorverbindingen in de Centrale Pyreneeën.

De lucht-bodem verdeling van PAKs op Tenerife geeft het belang aan van roet koolstof in de transfer van PAKs naar de plaatsen boven de inversielaag. Ook in de Europese hooggebergten worden de POP in de bodem goed weergegeven door de POP in de aërosols. Desalniettemin worden POP beter behouden in de sedimenten van de hooggebergtemeertjes. Verticale profielen van de sedimenten tonen een significante toename van POP niveaus aan het eind van de tweede helft van de 20ste eeuw, wanneer de productie en gebruik van deze componenten op gang komt, en een significante afname vindt plaats in de laatste jaren, wat een contributie kan zijn van de het beleid op schonere lucht en verbeterde verbrandingstechnieken.

Een model voor atmosferische PCB congeners op wereldschaal is verder geformuleerd. Dit model evalueerd de degradatie van PCBs door OH-radicalen en hun geschatte troposferische verblijftijden.

Alle vermelde resultaten in deze thesis zijn gepresenteerd in de vorm van wetenschappelijke artikelen die gepubliseerd staan, ter perse liggen, of gerecenceerd worden voor publicatie.

Resum

Els compostos orgànics persistents (COPs) com l'HCB, els PCBs, els DDTs, els HCHs, els endosulfans i els HAPs, són contaminants ubicus distribuïts per tot el planeta. La majoria d'ells foren sintetitzats per beneficiar el desenvolupament humà, sense tenir en compte la seva resistència a les degradacions biològiques, químiques i físiques, la seva capacitat d'acumulació en material orgànic i la seva toxicitat.

En la present memòria de tesi s'estudia el paper de l'atmosfera en la distribució ambiental dels COPs en les àrees remotes de muntanya i els destí d'aquests compostos en els sòls i els sediments dels llacs d'alta muntanya. S'han estudiat els COPs en la troposfera subtropical de Tenerife i l'atmosfera de l'alta muntanya europea (Pirineus centrals i Tatres altes) es troben dins del marge inferior dels observats en altres atmosferes remotes. En tots els llocs d'estudi, la majoria de COPs estan ben homogeneïtzats dins l'atmosfera, tot indicant la importància del transport atmosfèric a llargues distàncies (LRAT) com a mecanisme principal de transferència d'aquests compostos cap a les zones remotes. A part d'un mostratge actiu amb l'aparell HiVol, s'ha realitzat un mostratge passiu de l'atmosfera amb fulles de *Pinus uncinata* i amb membranes semipermeables (SPMDs), que ha permès estudiar la distribució espaial i temporal dels compostos organoclorats en els Pirineus centrals.

La partició aire-sòl dels HAPs a Tenerife mostra que el sutge és el factor principal en la transferència de HAPs als sòls per sobre la capa d'inversió. L'alta muntanya europea també mostra una bona correlació entre les concentracions de COPs en els sòls i els aerosols. De tota manera, els COPs es conserven millor en els sediments dels llacs. Els perfils sedimentaris verticals mostren un augment significatiu dels nivells de COPs a finals de la segona meitat del segle XX, quan la producció i l'ús d'aquests compostos començava, i una disminució en els últims anys, probablament deguda a la contribució de les polítiques de control de la qualitat de l'aire i a la millora de les tècniques de combustió.

Addicionalment, en aquesta tesi s'ha formulat un model de distribució atmosfèrica dels congèneres de PCBs a escala global que pren consideració dels fenòmens de degradació d'aquests compostos per radicals OH i del temps de residència estimat dels PCBs en l'atmofera.

Tots els resultats esmentats es presenten en forma d'articles científics que ja han estat publicats o estan en procés de publicació.

Chapter 1 Introduction and Objectives

Chapter 1 Introduction and Objectives

1.1 Global Environmental Changes

Since the beginning of human development, the anthropogenic activities (hunting, burning of wood, agricultural activities, etc.) have left their mark on the environment. Nowadays, the increase and intensification of activities related to the industrialised society, with its unlimited demand and use of energy, have resulted in the environmental effects that are not anymore punctual and on local scale (near to the sites of production or/and application). The accumulation of effects due to human activities is generating global environmental changes. These processes can be observed in the presence of toxic compounds in the environmental compartments (water, soils and atmosphere) and its organisms, from remote environments, like the Polar regions and high-mountains areas (AMAP 1998; Grimalt et al.2001). Under the concept of Global Environmental Changes one can include problems like global climate change, destruction of the ozone layer, irreversible loss of biodiversity, desertification, acidification, and contamination of air, water, soils and organisms due to human activities. The chemical substances responsible for many of these problems can be defined as global contaminants and they include among others:

- CO_2, CH_4 and other greenhouse gasses.
- SO_4^{-2}, NO_3^- and other compounds causing acid rain.
- Chlorofluorocarbons (CFC) and other gasses that destroy the ozone layer.
- Radioisotopes, like ^{137}Cs, ^{14}C, and ^{90}Sr, generated during nuclear trials.
- Heavy metals, like mercury and lead.
- Persistent organic pollutants (POP), like the polycyclic aromatic hydrocarbons (PAH) and the semi-volatile organochlorine compounds (SOC), such as polychlorinated biphenyls (PCB), DDT, hexachlorohexanes (HCH), hexachlorobenzenes (HCB), and endosulphanes.

The environmental effects caused by the POP are a direct consequence of their toxicity, stability and resistance against physical, chemical, or biological degradation. Most of the studied compounds, except PAH, are man-made or xenobiotic. They did not appear in the environment until men made them. Since the ´40s of the 20th century, when the production and use started, these very useful compounds have been introduced in large quantities to the environment, where they have caused unforeseen harm. The intensification of the industry in the last century has increased the input of PAH to the environment to levels that have seriously affected the environmental health. It took until the late ´60s when the negative effects of organochlorine compounds were acknowledged. Nevertheless, it was already at the beginning of the ´60s that Rachel Carson rang the alarm bell in her thriller ´Silent Spring´ about the unlimited use of these compounds (Carson, 1962). Although her book lacks in scientific evidences, later investigations proved quite well most of her worries. In the last decades many POP have been banned in most industrialised countries.

Accordingly, decreases of levels have been observed in potential source areas where the chemicals were produced and used (Rapaport and Eisenriech, 1988; Eisenreich et al., 1989; Jeremiason et al., 1994; Gobas et al., 1995; Kjeller and Rappe, 1995; Sanders et al., 1995). Howerver, these compounds are still omnipresent in the environment and the observed decreases in remote areas are small if any (Baker and Eisenreich, 1990; Panshin and Hites, 1994; Hillery et al., 1997; Hung et al., 2001). Due to the specific environmental dynamics of POP, classical concepts like, 1) decrease of environmental impact with increasing distance from source, 2) dilution effect once entering into the open environmental, such as the atmosphere or water bodies, and 3) long-range transport increases dilution, may **not be true** for these compounds. The physico-chemical properties of POP may offer a net transference of the pollutants from sites where they were produced or applied, to sites where they were never used, without undergoing any important form of dilution. Several studies in the past decades have shown that POP are ubiquitous pollutants (Atlas and Giam, 1980; Iwata et al., 1993). Moreover, due to the semi-volatile character they tend to accumulate in areas of low ambient temperatures, such as the Polar and high-mountain regions (AMAP 1998; Grimalt et al., 2001) (Chapter 4).

This is of concern since most of the compounds cause toxic effects (Porta et al., 1999; Vreugdenhil et al., 2002) (Chapter 2). The United Nations have recently elaborated a programme on POP, which was also signed by the European Union (UNEP/GC 18/32, 1995, Aarhus (Denmark) 1998 i Stockholm (Sweden) 2001; Bulletin EU 5-2001: 1.4.41). In this programme they compel themselves to reduce or eliminate the production of certain POP, to prohibit their use, and to investigate the effects on the environment and human health. So, in less than 60 years after the first application strict regulations have been implemented to eliminate POP from the environment. The scientific community has the responsibility to clarify where the diffuse emission sources of POP are located, what their impact is on remote fragile ecosystems, where they will end up, and how long they will be in the environment. These investigations can help policy making upon them and other chemical compounds in the future, since it may be possible to point out the consequences of production and use of chemicals and to provide suggestions for prevention of their adverse effects.

The study of these compounds in remote high-mountain areas, where no application ever took place, makes it possible to improve the understanding of their global transport and environmental fate (Chapter 3 and 4). High-mountain areas are vulnerable to POP contamination because of

1) long residence times of persistent and lipophilic compounds in these oligothropic systems,
2) low volatility in cold climates,
3) thinner soil layers than in temperate and tropical areas,
4) slow biodegradation in soils and sediments due to low temperatures,
5) low sedimentation in lakes because of low annual primary production involving pollutant concentration thin sediment layers,

6) low species density, short food chains, and long lived animals in the top of the food chains which accumulate highly lipophilic contaminants in their bodies.

In the present study the role of the atmosphere in the distribution of POP in remote high-mountain areas is examined as well as the fate of these compounds in soils and lake sediments from these areas. Here fore, atmospheric, soil and sediment samples were collected and analysed in high-mountain areas from subtropical and temperate latitudes (Chapter 5). The atmosphere and atmospheric deposition data offered information on the transfer mechanisms of POP to these areas, while data from soil and sediment cores shows the historical input of the compounds. Both types of data sets are used to interpret the past and present degree of contamination of these remote mountain environments, and to interpret the interactions between the environmental compartments in these remote high-mountain sites (Chapter 6 and 7).

The studies presented in this thesis are part of larger European Community research projects dealing with the global transport and fate of POP (GLOBAL-SOC: *Global Mass Balance of Persistent Semi-volatile Organic Compounds*, project No: ENV4-CT97-0638) and the general environmental state of high-mountain lake areas (EMERGE: *European Mountain Lake Ecosystems: Regionalisation, Diagnostics and Socio-economic Evaluation*, project No: ENK1-CT1999-0032, http:\\www.mountain-lakes.com).

1.2 Objectives of the PhD-thesis

1) To measure and interpret the atmospheric background levels of POP in remote high-mountain areas on subtropical and temperate latitudes.

2) To measure and interpret the background levels of POP in soils and lake sediments from these areas.

3) To elucidate the mechanisms for the transport and fate of POP in remote high-mountain areas.

4) To understand the actual state of POP contamination on a regional and global scale.

Chapter 2 Persistent Organic Pollutants (POP)

Chapter 2. Persistent Organic Pollutants (POP)

As mentioned already in the introduction POP are toxic chemical compounds, which are widespread over the world surface, becoming ubiquitous pollutants. However, each group of these compounds was manufactured for different purposes, used preferentially in different locations and has specific physico-chemical properties that have resulted in distinct distribution patterns. In this chapter the studied compounds are described. *A priori*, they can be separated in two groups. The man-made organochlorine compounds (see 2.1) and the natural polycyclic aromatic hydrocarbons (see 2.3).

2.1 Organochlorine Compounds (OC)

OC are man-made toxic chemical compounds that encompass a wide range of chemical compounds with different structures and purposes. Here, only two groups are described: pesticides and industrial products.

OC pesticides (see 2.1.1) were initially produced to protect crops and human beings. Their input to the environment corresponds to the times related to their application in agriculture, and is often related to the crop growing season and pest outbreaks. Nevertheless, these products can also enter into the environment when they are not stored adequately.

Industrial OC (see 2.1.2), here only polychlorinated biphenyls, were produced to be used, for example, as dielectric fluids and flame retardant materials in industrial processes and products. Their input to the environment was often related to diffusion into the atmosphere or seepage to groundwater after application.

Despite these different origins and uses both OC types have in common their resistance against physical, chemical and biological breakdown. In addition, their high number of chlorine atoms make them highly soluble in lipids and less soluble in water, tending to accumulate in body tissue. The persistence and toxicity of these compounds depend on the amount of chlorine atoms and their position in the molecule. During 1970s most western countries (where most of the products were produced and used) started to ban the manufacture and use of most of these compounds. Nevertheless, present use in closed installations, inadequate storage or waste-dumps still form potential sources of these toxic compounds for entering the environment. Nowadays, most of them are classified by the United Nations as Persistent Organic Pollutants (POP), (UNEP/GC 18/32, 1995 and http://www.chem.unep.ch/pops/).

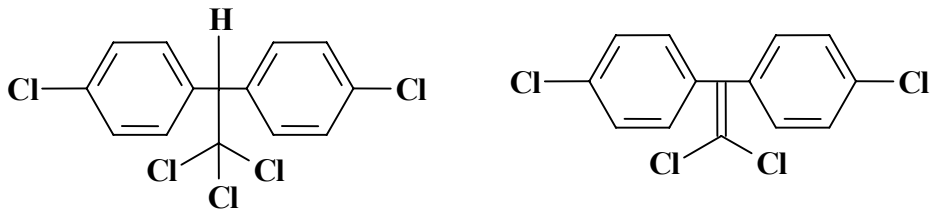
2.1.1 OC pesticides

OC pesticides were produced as insecticides, acaricides or nematicides for the protection of agriculture crops and human beings, but their persistence and non-species specificity caused several adverse effects in non-target species. The application of pesticides is often directly related to the

growing season of crops, or the pest outbreak. In this way the usage of pesticides is often season-related. The use of most of these products is nowadays prohibited, but they are still present in the environment. The following description of OC pesticides focus on the compounds that have been detected in the samples presented in this PhD-thesis.

2.1.1.1 *4,4'*-DDT and *4,4'*-DDE

Technical DDT (dichloro-diphenyl-trichloro-ethane) consists of more than 70% of the *para, para- (4,4')* -isomer and less than 30% of the *ortho, para*-isomer (Niesink et al., 1996). DDT was synthesised in 1874, but its "benefit" for crop protection was discovered in the late 1930s, leading to a Nobel Prize in 1948 for Paul Müller (Carson, 1962). The chemical was used since then for all kinds of purposes. It enters rapidly the cuticula of the insect where it provokes a violent stimulation of nerve impulses that eventually causes death. By the end of the 1960s it was realised that this chemical, and its metabolites DDD and DDE, were present in considerable levels in non-target species, causing serious toxic effects (Jensen 1966; Jensen et al., 1969). Especially the *para,para* (*4,4'*) configuration of this family (Figure 1) is held to be responsible for the adverse effects.



1) 2)

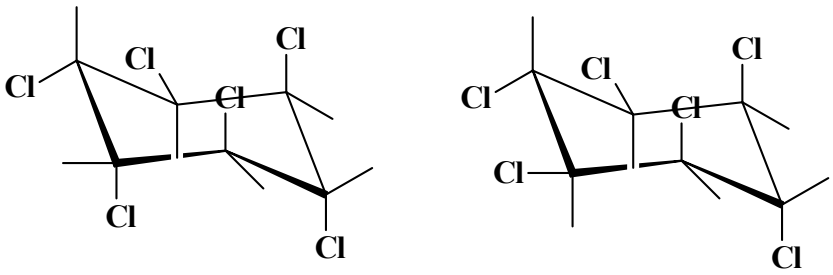
Figure 1. Molecular structures of 1) *4,4'*-DDT and 2) *4,4'*-DDE

DDTs are easily assimilated by organisms and adsorbed by soils and sediments, due to their high solubility in lipids, low solubility in water and high stability. DDE is more persistent than its parent DDT, and is still found in considerable amounts in high trophic levels and sediments in remote sites (Iwata et al., 1993; Newton, 1979). It is related to eggshell thinning, embryo-toxicity and failures in reproductive success of birds. For instance the peregrine falcon (*Falco peregrinus*) is considered to be very sensitive for DDE in its reproductive success (Newton, 1979; Steidl et al., 1991).

In the last 20 years many countries have banned the use of DDT by law, but in some parts of the world, like in many African countries, India and Mexico, it is still used as pest control for human diseases, like malaria and locusts pest (Douthwaite, 1991). Recently, a relationship was found between the exposure of *4,4'*-DDE and *4,4'*-DDT and the mutation of the K-ras gene in exocrine pancreatic cancer patients (Porta et al., 1999). Some physico-chemical properties of DDTs are summarised in Table 3.

2.1.1.2 HCHs

Pesticides like HCH (hexachlorocyclohexane) were originally a mixture of different compounds (Figure 2).



1) 2)

Figure 2. Molecular structures of 1) α-HCH and 2) γ-HCH

HCH contains five isomers, α-, β-, γ-, δ-, ε-HCH, of which γ-HCH is the one having insecticide properties. Although it is toxic, its half-life in tissue, eggs and other environmental compartments is relatively short in comparison to other pesticides. It breaks down readily into chlorobenzenes and chlorophenyls. Photoisomerization of γ-HCH to α-HCH is probable (Walker et al., 1999). γ-HCH and its metabolites have relatively high water solubility, so they can be washed out from the atmosphere relatively rapidly by rain. Furthermore, animals rapidly excrete them.

All HCH congeners are toxic to mammals. Chronic exposure has been related to adverse health effects in humans, such as immunosuppresion and neurological problems. α-HCH is the isomer which exhibits most carcinogenic activity. Together with technical-grade HCH (65% α-HCH, 8% β-HCH, 13% γ-HCH, 8% δ-HCH, and 3% ε-HCH) it has been classified as a probable human carcinogen Group B2 by the USEPA (United States Environmental Protection Agency). β-HCH has the tendency to bio-accumulate, which is a cause of concern as some studies indicate that this isomer may act as environmental oestrogen (Walker et al., 1999).

The first production started in 1943. And the production of the technical-grade HCH, which is mainly produced for developing countries, is estimated to be 550.000 t. The production of lindane (γ-HCH), for use in developed countries, is estimated to be 720.000 t. However, there are estimations on global productions of technical-grade HCH over 10 million t in the period of 1948 until 1997. Nowadays the large scale production and use of technical-grade HCH is strongly reduced due to the prohibition of the use. However, γ-HCH is still produced and used (Walker et al., 1999). Some physico-chemical properties of these compounds are summarised in Table 3.

2.1.1.3. HCB

HCB (hexachlorobenzene) (Figure 3) was used mainly as fungicide in wood and seed for crop production. However, it is also a by-product of several chlorinating procedures in manufacture of organochlorine solvents and can be found in plastics. Total estimated global emission is 23.000 kg yr^{-1} with a range between 12.000 – 92.000 kg yr^{-1} (Bailey, 2001).

It is almost insoluble in water, but evaporates very rapidly after release. Due to the high vapor pressure it is preferably found in the atmosphere where it can be transported over long distances. Nowadays this compound is banned, but is still delivered to the environment as by-product. HCB has shown to be acute toxic for men when in Turkey, between 1955 and 1959, it caused an outbreak of *porfiria cultanea tarda* after intake of contaminated food. Further on, there is a relationship between tyroid cancer and chronic exposure of HCB (Grimalt et al., 1994). Some physico-chemical properties of HCB are summarised in Table 3.

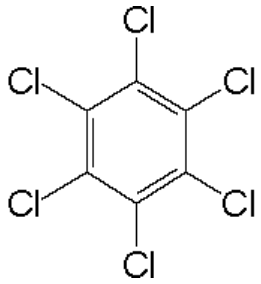


Figure 3. Molecular structure of HCB

2.1.1.4. Endosulphanes

Enosulphane, also known as thiodan, is an insecticide used in a wide range of applications to protect cereals, coffee, cotton, fruit, oilseed, potatoes, tea and vegetables against ´vandalism´ of insects. The technical mixture contains approximately 70% α-endosulphane (also called endosulphane-I) and 30% β-endosulphane (also called endosulphane-II) (Figure 4). As a consequence of this composition and the physico-chemical properties, the α-isomer is more abundant in the environment than the β-isomer and is easily transported through the atmosphere. The oral LD_{50} for technical endosulphane ranges between 18 and 355 mg kg^{-1} body weight, which makes it one of the most toxic chlorinated insecticides. In 1988, the world's production of technical endosulphane was about 10.000 t yr^{-1}. Because of its semivolatility (vapor pressure = 6.2 x 10^{-3} Pa) and photolytical stability in water, endosulphane is ubiquitous in the environment (Burgoyne and Hites, 1993). Some physic-chemical properties of these compounds are listed in Table 3.

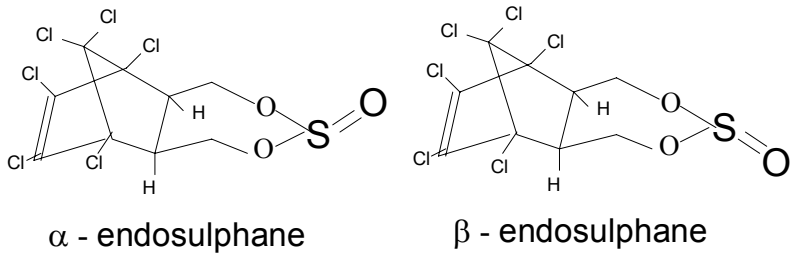


Figure 4. Molecular structure of α- and β-endosulphane.

2.1.2 Industrial OC: Polychlorinated biphenyls (PCBs)

PCBs were industrial compounds used as industrial fluids, dielectric fluids, heat transfer fluids, organic solvents, flame retardants, plasticizers, sealants and surface coatings. Between 1930 and 1975 around 635.000 t were produced in the United States. Worldwide production is estimated to be 1.3 million t. of which 97% was used on the Northern Hemisphere (Breivik et al., 2002).

In commercial PCB mixtures, the amount of chlorine atoms in the biphenyls depends on the duration and the temperature of the chlorination process. After purification the mixtures were commercialised under different names. For example, Arochlor (Monsanto, USA) or Clophen (Bayer, EU). The chlorine atoms can substitute the *para, meta* and/or *ortho* positions of the biphenyls. There are 209 congeners that contain two phenyl groups and one or more chlorine substituents. In this way PCBs can be divided into nine isomeric groups and one deca-chlorobiphenyl, all with an empirical formula of $C_{12}H_{10}$-nCln (n=1-10) (Figure 5; Table 1). Some physico-chemical properties of PCBs are summarised in Table 3.

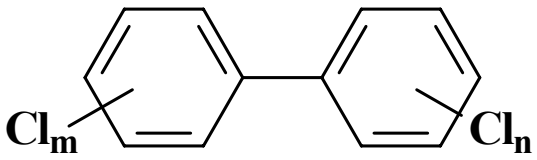


Figure 5. General molecular structures of PCBs.

PCBs were found for the first time in the environment by Sören Jensen, who detected the contaminants in pike from Swedish waters (Jensen, 1966). Within few years the adverse effects in organisms were recognised. Then their use and production were reduced (Safe, 1991, de Voogd et al., 1990) and finally banned in late 1970s in most industrialised countries.

PCBs are discharged into the environment by leaks from hydraulic, or industrial systems, diffusion out of coatings, or other products during production, waste incineration, or disposal, or after accidents. The levels of individual congeners differ from location and environmental compartment. Atmospheric PCBs are present predominately in the gas phase. However, the more chlorinated congeners are also present in the particulate phase (Pankow, 1987). There are evidences

that atmospheric PCBs are degraded by OH-radical reaction (Anderson and Hites, 1996a). However, the degradation rates are under environmental conditions have not been determined to date. The study these contaminants in remote atmospheres, such as the free-troposphere or high-mountain areas, may give insight into this question.

Table 1. Summary list of PCB congeners [o)] (Guitart et al., 1993; de Voogd et al., 1990)

Structural formula	Name (chloro biphenyl)	Nº of isomers	IUPAC systematic numbering	Mol. wt	% Cl	Nº of isomers identified in commercial mixtures
C12H9Cl	Mono	3	1-3	188.65	18.79	3
C12H8Cl2	Di	12	4-5	233.10	31.77	12
C12H7Cl3	Tri	24	16-39	257.54	41.30	23
C12H6Cl4	Tetra	42	40-81	291.99	48.65	41
C12H5Cl5	Penta	46	82-127	326.43	54.30	39
C12H4Cl6	Hexa	42	128-169	360.88	58.93	31
C12H3Cl7	Hepta	24	170-193	395.32	62.77	18
C12H2Cl8	Octa	12	194-205	429.77	65.98	11
C12HCl9	Nonta	3	206-208	464.21	68.73	3
C12Cl10	Deca	1	209	498.66	71.10	1

o) the corrected Ballschmiter and Zell nomenclature (Guitart et al., 1993) is used throughout the whole report.

Table 2. Selected PCB congeners

Nº	Molecular structure
18	2,2',5-triCB
28	2,4,4'-triCB
52	2,2',5,5'-tetraCB
70	2,3',4',5-tetraCB
90	2,2'3,4',5-pentaCB
101	2,2',4,5,5'-pentaCB
105	2,3,3',4,4'-pentaCB
110	2,3,3',4',6-pentaCB
118	2,3',4,4',5-pentaCB
123	2,3,4,4',5-pentaCB
132	2,2',3,3',4,6'-hexaCB
138	2,2',3,4,4',5-hexaCB
149	2,2',3,4',5',6'-hexaCB
153	2,2',4,4',5,5'-hexaCB
158	2,3,3',4,4',6-hexaCB
160	2,3,3',4,5,6-hexaCB
180	2,2',3,4,4',5,5'-heptaCB
194	2,2',3,3',4,5,5',6'-octaCB
199	2,2',3,3',4,4',5,5'-octaCB

The position of the chlorine atoms in the molecule is important for PCB toxicity. They are more toxic when the *ortho* positions of the molecule are not substituted, e.g. PCB#77 (3,3',4,4'-tetraCB), PCB#126 (3,3',4,4'5-pentaCB) and PCB#169 (3,3',4,4',5,5'-hexaCB). In these conditions the two phenyl groups can freely rotate and align following a flat structure (planar or coplanar PCBs). *Mono-ortho* and *di-ortho* PCBs (with the 2 and 2' positions substituted) are less toxic (de Voogd et al., 1990). Reported biological effects on terrestrial animals exposed to PCBs involve liver

damage, dermal disorders (chloracne), reproductive toxicity, thymic anthropy, body weight loss, immunotoxicity and teratogenicity and induction of several cytochrome P-450 (enzyme) isosystems (de Voogd et al., 1990). Although the application of these products is restricted or prohibited for many years now, they still cause toxic effects at trace level, as shown a study on Dutch school children (Vreugdenhil et al, 2002). The 19 PCB congeners selected for study in the context of the present PhD-thesis are reported in Table 2. These congeners are representative for the overall PCB abundance in the different environmental compartments. Some physico-chemical properties of these compounds are summarised in Table 3.

2.2 Polycyclic Aromatic Hydrocarbons (PAH)

PAH are compounds that consist of C and H atoms, grouped in the form of fused benzene rings. They are generally produced in all sorts of combustion encompassing from fossil fuels, to organic materials, such as vegetation. PAH composition depends on the combusted organic material and the temperature at which combustion takes place (Howsam and Jones 1998). Larger molecules of high molecular weight are easily generated at lower temperatures due to lower combustion efficiencies. Thus, combustion of diesel oil produces relatively higher molecular weight PAH than gasoline in vehicular engines (Khalili et al, 1995). In the late 19th century and early 20th low temperature coal combustion was the major source of PAHs. Nowadays fossil fuels, like gas, are used, which generate less PAHs. Diagenetic processes produce PAH as well. But their contribution is of smaller importance than pyrolytic sources on the global PAH concentration.

PAH enter primarily into the environment by atmospheric emissions, and are atmospherically transported easily over long distances. In this way they become ubiquitous contaminants arriving to remote areas where they are not produced (Wania and Mackay, 1996), but may cause damage to the ecosystem. Some PAH and their metabolites are tetratogenic and mutagenic, like benzo[a]pyrene (Howsam and Jones 1998). Increases in the PAH concentrations in remote European high mountain lake sediments since the late 19th century reflect the increase of fossil fuel combustion due to intensification of industrial activities. In these lakes PAH exhibited highest concentrations between 1960 and 1980 and stabilised after 1980s (Fernández et al, 2000), probably caused by the effect of legislative restrictions and improvements in combustion technology.

In late 1970s the United States Environmental Protection Agency (USEPA) listed 16 PAH as 'Priority Pollutants'. This list was later adopted by the European Union. However, a much larger number of PAH are emitted to the environment in combustion processes, but research on the emissions and environmental fate of PAH has tend to focus on these 16 compounds (see Figure 6 for 13 selected parent PAH analysed in this PhD-thesis and Table 3 for some physico-chemical properties). These PAH encompass a wide range of properties. In general, fluoranthene and higher molecular weight PAH tend to bound to atmospheric particles while the lower molecular weight

PAH are preferably transported in the gas phase, due to the higher vapor pressure (Pankow 1987; Pankow and Bidleman, 1992)). Further on, lighter PAH are more vulnerable to direct or indirect photo-degradation by OH radicals, as a consequence of their free movement in the gas phase, than the particle bounded PAH that are protected by the particles (Brubaker and Hites, 1998).

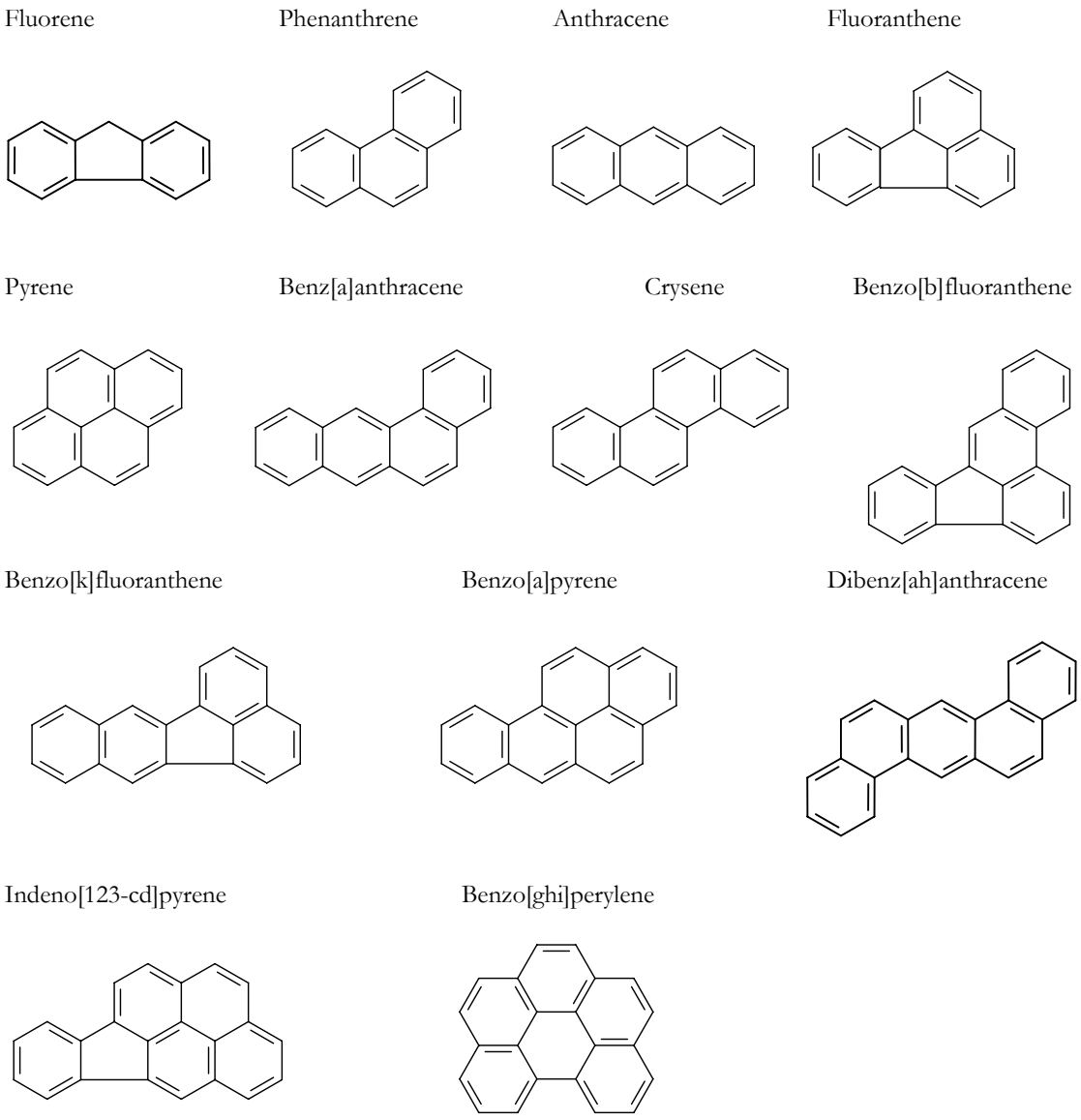


Figure 6. Molecular structures of studied PAHs

The particles that are directly related to the emission of pyrolytic PAH are black-carbon (BC). BC is produced by incomplete combustion of fossil fuels and vegetation fires. Like PAH it occurs ubiquitously. It can account for about half of the total organic carbon in certain soils. Structurally, BC may be essentially differentiated between soot-carbon (small particle size; SC) and char/charcoal. The former originate during the condensation of hot combustion gases involving free radical reactions of acetylene species leading into PAH, macro PAH, and SC. Conversely,

charcoal originates from incomplete combustion of plant tissue and diagenesis (Gustafsson et al, 2001) and always contains a core of unburned biomass material (with cell structure frequently discernible). During the past few years, the study of SC as a strong sorption matrix has received increasing attention (Bucheli and Gustafsson, 2000; Dachs and Einsenreich, 2000; Gustafsson et al., 2001). Adsorption onto SC has been shown to affect significantly the overall PAH sorption to sediments and aerosols. Since there seems to be a direct relationship between PAH and soot-carbon it is of interest to study the importance of this relationship in remote areas in order to understand the transport and world wide distribution of these pollutants.

Table 3 Selected physico-chemical properties of studied POPs at 278 K (Cotham and Bidleman, 1989); Ballschmiter and Wittlinger, 1991; Fischer et al., 1991; Guerin and Kennedy, 1992; Mackay et al., 1992; ten Hulscher et al., 1992; Dunnivant et al., 1992; Hargrave et al, 1997)

POP	Mol Wt.[a]	P_L [b]	Log K_{ow} [c]	H [e]
Fluorene	166	0.72	4.2	7.9
Phenanthrene	178	0.11	4.6	3.2
Anthracene	178	7.8×10^{-2}	4.5	4.0
Fluoranthene	202	8.7×10^{-3}	5.2	0.6
Pyrene	202	1.2×10^{-2}	5.2	0.9
Benz[a]anthracene	228	6.1×10^{-4}	5.9	0.6
Chrysene	228	1.1×10^{-4}	5.9	0.2
Benzo[b j]fluoranthene	252		5.8	0.15
Benzo[k]fluoranthene	252	4.1×10^{-6}	6.0	0.11
Benzo[a]pyrene	252	2.1×10^{-5}	6.0	0.045
Indeno[123-cd]pyrene	276			
Dibenz[ah]anthracene	278	9.2×10^{-8}	6.8	0.069
Benzo[ghi]perylene	276	1.4×10^{-8}	6.5	0.076
HCB	285	3.1×10^{-3}	5.5	53
Alpha-HCH	181	7.3×10^{-3}	3.9	0.10
Gamma-HCH	181	1.9×10^{-3}	3.9	0.061
Alpha-endosulphane		6.2×10^{-3}	3.6	1.07
Beta-endosulphane		3.2×10^{-3}	3.6	0.04
4.4'-DDT	165	3.8×10^{-5}	6.0	6
4.4'-DDE	235	8.6×10^{-4}	5.7	34
PCB18	257	8.0×10^{-2}	5.6	32
PCB28	257	2.0×10^{-2}	5.8	29
PCB52	292	1.0×10^{-2}	6.1	32
PCB70	292	6.0×10^{-3}	6.3	17
PCB101	326	3.0×10^{-3}	6.4	25
PCB110	326	2.0×10^{-3}	6.3	20
PCB138	361	5.0×10^{-4}	7.0	13
PCB153	361	2.0×10^{-4}	6.9	17
PCB180	395	1.0×10^{-5}	6.9	11
PCB194	430	1.0×10^{-5}	7.6	29

[a] - molecule weight (a.m.u.);
[b] – sub-cooled liquid vapor pressure (Pa);
[c] – natural logarithm of the octanol – water partition coefficient;
[d] – Henry's Law Constants (Pa m^3 mol^{-1}),

Chapter 3 Sampling sites in high-mountain areas

Chapter 3 Sampling sites in high-mountain areas

In the past and even nowadays high-mountain environments were regarded in awe by men. Hostile meteorological conditions, thin air, lack of vegetation, and difficult access made them considered to be homes of Gods and mythological spirits, as did belief the ancient Greek with Mount Olympus, the Norwegians with Jotumheimen (´Home of Ice Giants´), and the Tibetans with Chomo Longmu (Mount Everest) (´Mother of Mountains´), etceteras. At least they were no safe place for men, who limited their settlements to the valleys at lower altitudes. Scientific interest in mountain systems did not begin until mid-nineteenth century, although the first measurements of meteorological changes with altitude came much earlier. In September 1648 the effect of altitude on pressure was proved by Florin Périer, who operated a simple Torricelian mercury tube at the summit and base of Puy de Dôme, France, on request of his brother-in-law Blaise Pascal. And the French engineer H.B. de Saussure made observations of relative humidity during an ascend of Mont Blanc in August 1787. A year later he made developments on the temperature lapse rates in this area. After 1850 meteorological, geological and biological measurements began to be made systematically. It is in this period when different meteorological stations are established in European mountain regions. Through the years more stations were built in remote mountain areas all over the world. Besides the standard meteorological data, e.g. temperature, pressure, wind speed and precipitation, most of these stations are equipped nowadays with instruments for the analysis of solar radiation, aerosols, trace gases, like CO_2 , and POP. This is, for example, the case for the high altitude observatories of Izaña (2367m; Tenerife) and Mauna Loa (3399m; Hawaii). One of the lastest features on atmospheric observations is the installation since 1989 of the high altitude Pyramid Laboratory in the Khumbu Valley of the Himalayas at an altitude of 5050m (Barry, 1992; Baudo et al., 1998).

Besides areas of scientific interest, nowadays the mountain regions nowadays are the majestic scenery for recreation and wilderness resources. In the recent years a number of international organisations, like the United Nations (UN) and the Inter-governmental Panel in Climate Change (IPCC), are devoting increasing attention to mountain issues, in order to protect and conserve these vulnerable areas. A specific point was also included in the Plan for Action into the 21st Century (Agenda 21 – Chapter 13) giving to mountain regions a priority in the global environmental-development agenda equal to that of other global change topics, such as climate change, desertification, or deforestation. Mountain regions have continued to move up in political and scientific agendas, and the UN dedicated 2002 as the International Year of the Mountains. Mountains are important. They contain unique vegetation and wildlife. They provide major freshwater deposits for water consumption and hydroelectric power generation. They often contain large forest reserves and sometimes contain valuable mineral resources. All together they cover around 20% of the earth's land surface, but little is known about the state of contamination. Nevertheless, recent international environmental research projects, like the European Community

financed projects AL:PE (*Acidification of Mountain Lakes: Paleolimnology and Ecology*), MOLAR (*Mountain Lakes Research*), and EMERGE (*European Mountain Lake Ecosystems: Regionalisation, Diagnostics and Socio-economic Evaluation*) have shown that the mountain systems may be remote but they are not at all pristine. They suffer from input of toxic chemical compounds, which could cause adverse effects on these fragile ecosystems.

The studied mountain areas in this PhD-thesis are separated into high-mountain ranges situated in the subtropical troposphere (e.g., the Island of Tenerife with the mountain of Teide) and the European continent (e.g., the Central Pyrenees and the High Tatras) (Figure 7). The separation of the areas is based on their different geographical situations and, as a consequence, different climatological conditions.

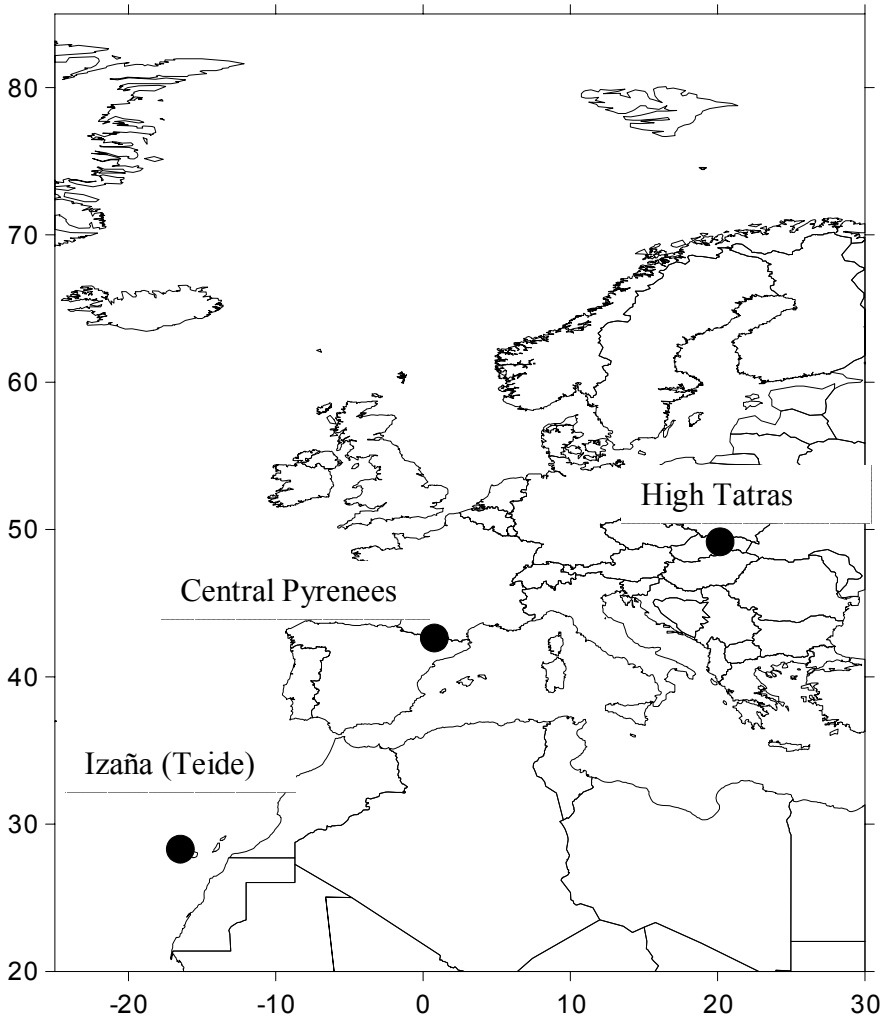


Figure 7. Geographical situation of the three studied high-mountain regions

3.1 Subtropical troposphere

3.1.1 The Island of Tenerife

The Island of Tenerife (28°18´N, 16°29´W) is the largest island (2057 km²) in the Canary archipelago. The distance from Tenerife to the African and European continent encompass ca. 350 km and 1300 km, respectively. The Canary Islands form, together with the Azores, Madeira and the Cap Verde, a triangle in the subtropical zone of the Atlantic Ocean called Macaronesia. All these islands have a volcanic origin (Castellano-Gil and Marcías, 1993). The highest volcano can be found in Tenerife, Teide (the place ¨where hell is vomiting fire¨).

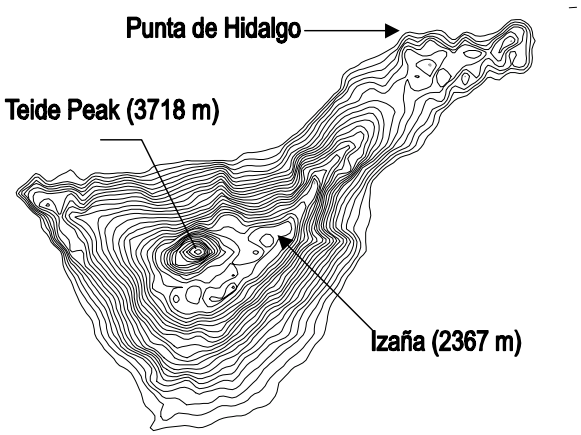


Figure 8. Island of Tenerife and atmospheric sampling sites.

The volcano of Teide, which rises up until 3718 masl, dominates Tenerife. In fact, the large environmental differences between the northern part of the island and the southern part are caused by its presence. The south side is arid, the north side is humid and green. Atmospheric samples were collected at the Atmospheric Observatory of Izaña (2367m) near the peak of Teide and at the lighthouse of Punta Hidalgo (40m) on the north-eastern side of the island (Figure 8). Soil samples were collected both on the northern and the southern slopes from sea level up to 3400m.

3.1.2 Soils and vegetation

The soils of the Island of Tenerife are derived from volcanic ashes. In general they can be classified in three groups: sandy entisols in the Northern coastal area up until 600m, the inceptisols in the middle of the island, between heights of 800 and 1800m, and the pumice stone entisols above the local tree line (>2000m) (Fernández et al., 1982).

The island of Tenerife has many different ecosystems, which contain many endemic species, depending on its specific climate and relief. These conditions involve coastal ecosystems, where vegetation is under constant stress of strong winds and salt. These are the habitats of plant

species like ´lechuga marina´ (*Astydamia latifolia*), ´salado´ (*Schizogyne sericea*), ´balancón´ (*Traganum moquinii*) and ´uvas de mar´ (*Zygophyllum fonanesii*). In the higher areas of the coastal zone ´aulaga´ (*Launaea arborescens*) can be found. In the humid places of the southern part of the island, on the basalt layer there are the endemic species ´cardones´ (*Euphorbia canariensis*) and ´tabaibas´ (*Euphorbia sp.*). Relief and climate also create ecosystems like the one of the north-eastern part, Anaga Mountains, called after a Guanche queen. It contains cloud forests that can be considered as living fossils of the forests that before the quartenaire era of glaciers covered vast parts of Europe. Typical laurel species are the Canary laurel tree (*Laurus indica*), the ´til´ (*Ocotea forens*), the ´viñatigo´ (*Persea indica*) and the ´barbuzano´ (*Apollonia canariensis*). In the places where the forest was burnt down, or cut, another type of vegetation has developed, called Fayal-Brezal, characterised by the ´faya´ (*Myrica faya*) and the ´brezo´ (*Erica arborea*). Going up, from La Laguna to El Teide, one will pass the pinewoods, which are almost exclusively formed by the endemic Canary pine trees (*Pinus canariensis*). This species is adapted to the dry climate and is able to sprout after fires, or even recover itself after the fires. Above 1900 masl the landscape is occupied by bushes like ´laburnum´ (*Adenocarpus foliolosus*) and ´retama blanca´ (*Retama reatam*) (Castellano-Gil and Macías, 1993).

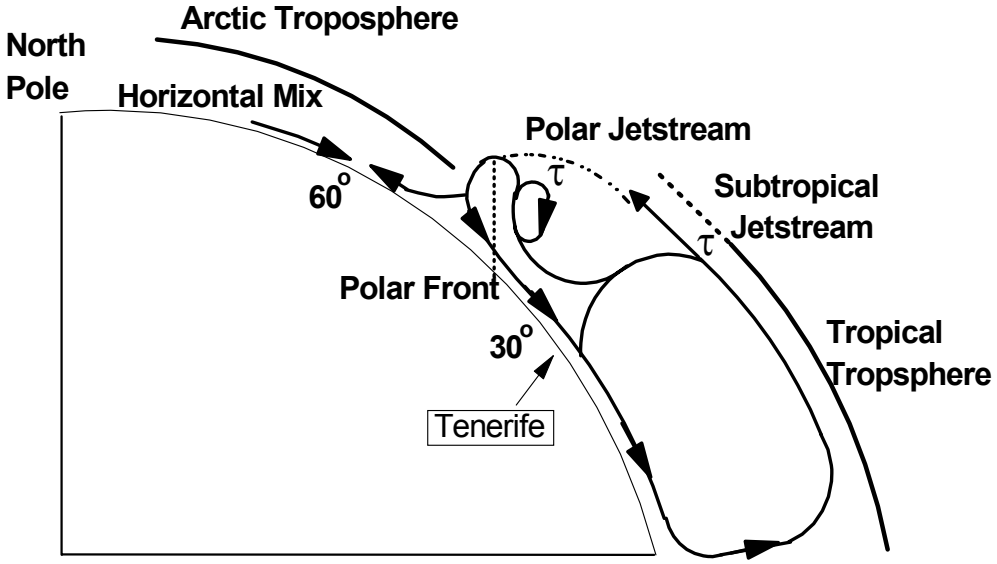


Figure 9. Hypothetical version of the heat/air mass circulation cells (adapted from Cuevas (1995))

3.1.3 Meteorological conditions

The local climate of Tenerife, and its different ecosystems, results from large-scale climatic phenomena, such as the circulation of heat/air from the equator to the poles. At the latitude of Tenerife (28°N) the circulation of the Hadley cell dominates the meteorology as explained below. This cell is located between the equator and both sides of the hemispheres up to 30°N and S (Figure 9). Due to the unequal irradiation, absorption, and reflection of sunlight on the world surface, there is a net gain of heat between 20^0N and S and a net loss of heat at the higher latitudes. These differences have to be compensated by a transfer of heat from the equatorial zones to the

higher latitudes by ocean currents. In addition the evaporation of water plays a smaller, but important role in the transport of heat on a global scale (Wells, 1997). The evaporation of water in the tropics causes rain fall and strong low air pressure bands in the lower atmosphere along the equatorial zone, mostly in the Inter-tropical Convergence Zone (ITCZ). These are the zones where the great tropical rainforests are situated. At latitudes of 30°N and S the ascended air from the tropics descends, causing relatively warm (high potential temperature) and dry air at these latitudes. Here, high-pressure areas, or anticyclones, are common and these are the zones of the largest deserts in the world (Cuevas, 1995; Open University, 1989). Ascending air masses along the equatorial zone and the descending air masses along the subtropics causes a pressure gradient between the subtropics (high) and the equator (low). Because of Earth rotation (causing the Coriolis force) and the friction of air at the surface, this air flow does not go straight in north-south direction, but in a general NE-direction in the northern hemisphere and a SE-direction in the southern hemisphere (Wells, 1997; Open University, 1989). In the days that Europeans (like Columbus) rediscovered the new worlds and the colonial trade started off, sailing vessels used these constant winds. In the English language this defined them operationally: trade winds.

These trade winds play a very important role in Tenerife. Because of the large and stable high pressure areas located around the Azores round the year (Azores high), wind comes from a dominated NE-direction. During their journey from the north-west coast of Africa and temperate zones in the direction of the ITCZ, the warm surface air from the continent is rapidly transformed by contact with the cooler surface water in a shallow marine boundary layer, or mixing layer. The moisture content of the mixing layer is rapidly increased by the water evaporation from the ocean, whilst sensible heat is lost from the air to the ocean because of the reversal of the temperature gradient (Wells, 1997). At the latitude of Tenerife the mixed layer has reached a thickness of around 1500m, and the surface air has more or less the same temperature as the sea surface, around 18°C. Because of the addition of water vapour and the net cooling low stratus clouds are formed in the mixed layer. The atmospheric sampling site at Izaña (2367m) is situated above this layer, while Punta de Hidalgo (40m) is situated within. In the north side of the island a field of stratus clouds can form especially during daytime, which is visible from above the mixed layer and is called ´Mar de Nubes´ (Sea of Clouds). This cloud field has its maximum frequency and extension in summer, when the evaporation of the seawater is highest and the trade winds are more intensive. The suppression of the marine boundary layer is further enforced by a strong temperature and humidity inversion. Above the marine boundary layer, the air has a high potential temperature and is very dry, representing the Free Troposphere. In contrast, the air in the marine boundary layer has a relative low potential temperature and high humidity. The two air masses are completely different (Font Tullot, 1956, Castellano-Gil and Macías, 1993, Cuevas., 1995, Wells, 1997). The trade wind inversion shows annual variation. Annual shifting of the subtropical highs causes annual variation in intensity of the trade wind inversion and altitude of the Sea of Clouds. In summer the inversion

is more intensive than in winter and the zone of the subtropical highs is situated at higher latitudes (45° N) causing an increase of relative humidity because of stronger and longer trade wind influences. Also soil warming during summer causes an extremely dry air mass above the boundary layer and forces the inversion between the two air masses. In winter the zone of the subtropical highs is situated at the latitude of Tenerife (27,5°N) (Cuevas, 1995), and the trade wind inversion is broken up frequently, because of the decreasing differences between the air masses. In these cases trade wind air can mix with the air of the Free Troposphere.

In the Free Troposphere, above the inversion layer, the influence of the Coriolis force and friction with the earth surface is small. At Izaña (2367m) the wind is coming predominantly from a NW-direction. In the summer months an anticyclone is frequently formed above north Africa and the island is situated between two high pressure areas (Font Tullot, 1956). This situation causes frequent invasions of dust from the Sahara in these months. However, in winter the sub-tropical jet stream (very strong westerly wind between the tropical and the moderate latitudinal tropopause) is located above Tenerife causing a very strong and cold NW wind, with air that has its origin in the sub-polar zone. The annual wet deposition over the period 1961-1989 at Izaña is around 500mm, with 69% of the precipitation from November until February.

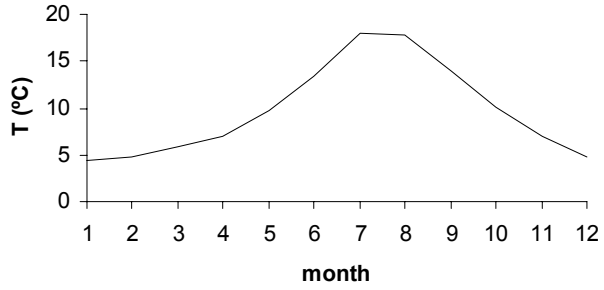


Figure 10. Average atmospheric temperature at Izaña (2367m) for the period between 1961 and 1989 (adapted from Cuevas (1995)).

In the period November - February the Sea of Clouds can reach the height of the observatory and causes precipitation in the form of rain or snow. The mountain can be completely covered with snow. In summer, however, it is extremely dry. Although the sky is covered 76 days of the year (mainly occurring in wintertime), Izaña has many sun hours (77% of its time). The average monthly temperatures at Izaña are shown in Figure 10.

3.1.4 Human activity

Since the 18th century travellers, scientists, naturalists and foreign businessmen have established themselves on the island. At the end of the 19th century the exportation of tourism became an interesting economic alternative. Hotels were built and several societies were established.

Due to different problems, e.g. world wars and economic depressions, tourism did not develop to its actual extent until the 1960s. This activity became a cultural phenomenon that greatly influenced the Canarian economy and environment.

In the 21st century Tenerife became a modern island whose economy was dominated by agriculture (especially wine and banana), trade, tourism and small-scale industries form the principal economy. Although, the island is quite populated there is practically no habitation above 1000m. People are concentrated along the coast. The most important industrial activities are a petrol refinery and a power plant located north-east and east of the Izaña Atmospheric Observatory, respectively. However, at both atmospheric sampling sites (lighthouse of Punta de Hidalgo and Izaña) and the soil sampling sites, the influence of the human activities can be neglected (Castellano-Gil and Macías, 1993; Cuevas, 1995).

3.2 European high-mountain areas

The two areas studied here, the Central Pyrenees and the High Tatras, are very similar in many aspects, such as geological formation, geomorphology of the lake basins and general climatological conditions. Both areas are part of larger mountain ranges, forming an important part of the orography of the European continent. Due to their extension, their complex orography, and their situation in the continent, they have major influences on regional and local climates. More over, they are located on temperate latitudes.

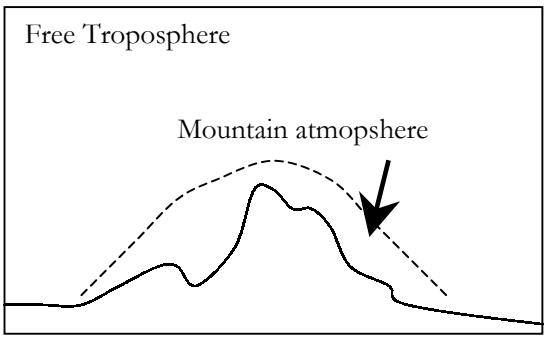


Figure 11. The mountain atmosphere. Adapted from Barry (1992).

In contrast to Conversely of the ´simple´ meteorological conditions of Tenerife, which rises up as a needle in the middle of the subtropical Atlantic Ocean, the atmospheric situation in the European high-mountains is much more complex. In these sites the atmosphere is not representative of the Free Troposphere, as in Tenerife, but of a Mountain Atmosphere (Barry, 1992) (Figure 11). Inversion or boundary layers are less defined as they were on Tenerife. In Europe, the Westerlies play an important role on the weather and wind patterns. These systems are associated with depressions or frontal cyclones from the Atlantic Ocean cause abundant precipitation in the north/western part of the European continent. In the continent, air masses find

obstacles like the mountain ranges, which generates an ascent. Descending air pressures with altitude result in descending air temperatures causing saturation of the water content of the air masses, and consequently altered precipitation. Depending on arrival of cold or warm fronts to the mountain ranges the precipitation can be more or less abundant. Furthermore, influence of low altitude air masses at higher sites depends on the type of front (Barry, 1992). These phenomena may cause smaller scale effects, like higher precipitation at higher altitudes, or at the slopes where the frontal cyclones find the mountain ranges, while on the other site of the mountain range dry air is descending. Furthermore, slopes may be heated up during daytime causing small scale low pressure zones, which result in air flows from lower parts of the valley to the mountain (valley-mountain breeze). Conversely, descending air temperatures at higher altitudes in the night-time may provoke a descending airflow from higher sites towards the valley (mountain-valley breeze). Stable atmospheric situations (high atmospheric pressure) often results in a temperature inversion, where cold (and often humid) air occupies the valley, while mountaintops are bathing in the sun. A sea of clouds is often visible in these cases, which is more persistent in wintertime (Barry, 1992).

The sites for atmospheric, soil and sediment sampling were all far away from potential local contamination sources. Thus, they can be considered as sites under the influence of long-range transport of contaminants. Nevertheless, regional scale meteorological conditions may affect their air quality.

3.2.1 Central Pyrenees: Estany Redon

The Pyrenees are situated in the connection of the Iberian Peninsula and the rest of the European continent and range from the Mediterranean Sea to the Atlantic Ocean over a length of about 435 km. Estany Redon is located in the Central Pyrenees, where the mountains reach their maximum height up to 3404m (Pic d´Aneto). The mountain range was formed around 50 Million years ago, when the Iberian landmass collapsed into the European continent. In the same period other alpine areas, like the High Tatras, the Alps and the Himalayas, were formed.

3.2.1.1 Geographical situation and origin of Estany Redon

Estany Redon (42°03´33,5´´N; 0°46´12,7´´E; 2240m) is an oligotrophic high mountain lake located in the Catalan part the Central Pyrenees. There is some confusion in the literature about the name of the lake. Redon is its correct name as it is in Occitane, the official language of Vall d´Aran, the county in Catalonia where Occitane and not Catalan is spoken. Sometimes it appears in the literature as Llac Redó or Redo, which corresponds to its Catalan name. In all cases, Estany Redon means ´round lake´. It is situated at the higher end of the valley of Noguera Ribagorçana, and forms one of the headwaters of the river with the same name. The lake is accessible by the two-lane

highway N-230 until the tunnel of Vielha, where the High Mountain Research Centre (CRAM; 1600m) is located. From this site the lake is reached by walking up in eastern and northern direction through the valley of Conangles and the Barranc del Redó, respectively, passing a forest of beech (*Fagus sylvatica*), silver fir (*Abies alba*), *Pinus uncinata* and finally high mountain pasture.

The basin of the lake is open in the southern direction and surrounded in the west by the Tuc de Port deth Vielha (2606m), in the east by Tuc de Sarraera (2632m) and Tuc de l´Estany Redon (2540m), and in the north by the ridge between the two highest summits. This range forms the divisor between the southern and northern slopes of the axial of the Pyrenees. The outflow of the lake, in southern direction, flows into the Barranc del Redó and the valley of Conangles to the Noguera Ribagorçana river. In this direction the altitude loses 600m in less than one kilometre.

Figure 12. Estany Redon in March and June 2002. Photos are taken from Tuc deth Port de Vielha in eastern direction.

The lake is formed by the activity of glaciers in the Pleistocene coming down from the Tuc deth Port de Vielha in eastern direction and from the Tuc de Sarraera in western direction. While in the north of the Northern Hemisphere whole landmasses were ice covered, in the southern parts only the mountain chains were ice covered. The lake is a glacial cirque that was feeding the glaciers that went down through the Vall de Conangles in the direction of the valley of Noguera Ribagorçana. The work of the glaciers in the past and the present climatic conditions result in a lake with a depth of around 70m and a surface of around 24 Hm^2. This makes Estany Redon one of the high mountain lakes in the Pyrenees with the largest volume (7.75 hm^3) (Catalan 1987; 1988).

3.2.1.2 Geomorphology, soils and vegetation

The amphitheatre-like shape of the basin is all granite (granodiorita of the Maladeta) corresponding to the late-hercinian intrusion. The whole catchment of the basin is 155Hm^2 from which 16% is occupied by the lake surface. Due to the activity of the ice, a threshold of rock blocks was formed in the southern part (the exit of the glacier). The whole basin shows a degraded image due to the intense dynamics of the ice. The lake does not have a principal entrance of water, but

multitude sources in the rocky catchment, most water is incorporated from direct atmospheric inputs. This explains the oligotrophic character of the lake. Further on its waters have low ion levels, which are just high enough to sustain the brown trout (*Salmo trutta*) community living in this lake (Table 4). In dry periods the lake does not receive water (Catalan 1987; 1988).

Three dominant types of land cover are found in the lake catchment; dry alpine meadows, moraines, and solid rock. Due to the steep slopes, the rock types and the cold climatic conditions the soils in the dry alpine meadows are poor developed (leptosol, histosol, and podsol) with a black acid humus layer and a mineral (sand) horizon of few centimetres thickness directly covering the bedrock. Lichen and mosses cover a considerable part of the rocky basin. Due to the geographical position and the altitude the basin contains alpine vegetation. The predominant species are *Festuca eskia* and *Carex sempervirens*, which are situated on the sun spotted sites and steep slopes. Further on, some individuals of *Rhododendro* and *Pinus uncinata* are growing sparsely and in bonsai form (Catalan 1987; 1988).

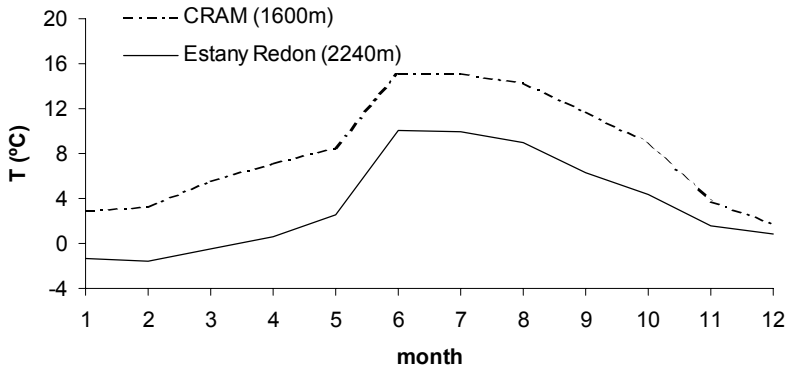


Figure 13. Average monthly atmospheric temperatures in 2002 at CRAM (1600m) and Estany Redon (2240m)

3.2.1.3 Meteorological conditions

The alpine climate of the valley and near the lake consists of cold winters and relatively cool summers. Figure 13 shows the average monthly temperatures at CRAM (1600m) and Estany Redon (2240m). The average annual temperature at Estany Redon is about 3.2ºC, while this temperature is around 8.8ºC at altitude of CRAM (1600m). The lake starts to freeze up normally around the beginning of December and stays ice and snow covered until late May (Figure 12). The yearly wet precipitation at Estany Redon is around 1500mm. In winter it is essentially constituted of snow. During the rest of the year precipitation is in the form of rain, but it is of less importance at this altitude (Catalan 1987; 1988). The air masses arriving to the sample site may have their origin on the European continent as well as the Atlantic Ocean. Now and then the site receives dust invasion from the Sahara (Camarero and Catalan, 1996).

3.2.1.4 Human activity

Besides the researchers visiting the lake basin, it is also visited now and then by excursionists. In some cases illegal trout fishing takes place. The lake is situated in a natural environment with human small scale human activities in the valleys. The valley of Noguera Ribagorçana, 600m below the lake in the south, contains few small villages. Senet at ±9km distance is the nearest by. Here there are no industrial activities. A two-lane highway N-230 is passing through the valley ending in a tunnel. On the other side of the mountain range, in the north, where the tunnel is ending, Vall d´Aran is located. Non of its villages has important industrial activities and no OC contamination is expected to arrive from these sites. In case of the PAH, combustion of wood in household fires and eventually forest fires are the two main possible sources. Further on, the incendiary of Vielha, located on the northern exit of the tunnel of Vielha (Vall d´Aran), could play a role in the PAH levels and composition, together with the traffic on the highway N-230 itself of course. However, besides these regional sources of small intensification and scale, the effect of the human activity concerning POP is considered to be low.

3.2.2 The High Tatras

These mountains are situated on the national borders of the Slovakian Republic and Poland (20°0`E, 49°4`N). The length is about 34km from east to west and the wide is about 10km, which makes it the smallest alpine area in Europe, with modest heights up until 2654m (Gerlachovský štit) and 2634m (Lomnický štit). The High Tatras, or Vysoké Tatray, form the highest part of the Carpatian range. The area is not only a National Park since 1949, it also has become a Biosphere Reserve under the UNESCO Man-and-Biosphere-program since 1993. Therefor, it receives special environmental protection.

3.2.2.1 Geographical situation and origin of the studied lakes

All studied lakes are situated above the local tree line, where glaciers in the past have formed amphitheatre-shape basins. The formation of the lakes as a consequence of the glacier activity is similar to that of Estany Redon. After the retreat of the glaciers about 10.000 yr. ago more than 100 lakes had been formed in the High Tatras. The soils and sediments of the oligotrophic lakes studied in this PhD-thesis are Dlugi Staw (49º13´36´´N; 20º00´39´´E; 1783m), Starolesnianske Pleso (49º10´48´´N; 20º10´04´´E; 2000m) and Ladove Pleso (49º11´03´´N; 20º09´46´´E; 2057m) (Table 4). The first lake is situated in the north-western (Polish) part of the High Tatras in the Gasienicowa Valley, which is open to the north-east. The last two lakes are situated on the south-eastern part of the range, in the Velká Studená Valley, which is open in the south (Figure 14). The atmospheric samples were collected at the meteorological observatory of

Skalnaté Pleso (49º06´36´´N; 20º08´24´´E; 1778m) of the Slovakian Meteorological Service (SAV), which is situated close to the later Velká Studená Valley.

Figure 14. Ladove Pleso and Starolesnianske Pleso in the valley Velká Studená Valley (Foto: Ladislav Jiroušek).

3.2.2.2 Geomorphology, soils and vegetation

The bedrock in all studied sites is granite. Three dominant types of land cover are found in the catchment: dry alpine meadows, moraines, and solid rock. Due to the steep slopes of the surrounding mountain peaks, rock types and cold climatic conditions, the soils in the dry alpine meadows are undeveloped (leptosol, histosol, and podsol) with a shallow organic horizon (0.05 – 0.17m; 0.14m) and 0.33m deep mineral horizon.

The vegetation in the High Tatras is marked by its great diversity in both horizontal and vertical gradients. Beech (*Fagus Sylvatica*), fir (*Abies alba*) and Norwegian spruce (*Picea abies*) dominate the (lower) mountain (sub)-montane) zone (up to 1250m). The upper mountain (supremontane) zone (up to 1550m) is almost completely covered by Norwegian spruce, European larch (*Larix decidous*), and arolla pine (*Pinus cembra*). The subalpine zone (up to 1800m) is covered with dwarf pines (*Pinus mugo*). This small pine tree species forms the tree line. The alpine zone is occupied by alpine tundra, formed by *Salix reticulata, Salix herbacea.* The vascular plants are getting scarce with altitude and the rocks are covered with lichens and mosses, of which the snow andreaea moss (*Andreaea nivalis*) is typical.

3.2.2.3 Meteorological conditions

The climate of the High Tatras is determined by their situation in the heart of central Europe and is characterised by a high degree of continentality. There are large differences between summer and winter temperatures and there is high precipitation in summer. The annual

atmospheric temperature at the summits is –3.8ºC. At the atmospheric sampling site of Skalnaté Pleso (1778m) the average annual temperature is 1.6ºC. Figure 15 shows the average monthly temperature over the period between 1930 and 1960 for Skalnaté Pleso (178m). The average temperatures in the warmest month, July; at 1018m, 1778m and 2634m are 14.4ºC, 10.0ºC and 4.2ºC, respectively. The temperature inversions are frequent in the air layers of valleys and basins. The mean annual precipitation increases with altitude from 650mm to 1350mm and 2200mm, at 1018m, 1778m and 2634m, respectively. The days of precipitation also increase with altitude being 190 days (90 days snowfall) at 1018m and 215 days (150 days snowfall) at 2634m (Lomnický štit). Between the altitudes of 1018m and 2634m the areas are snow-covered between 130 and 240 days. The studied lakes are normally frozen from November until June.

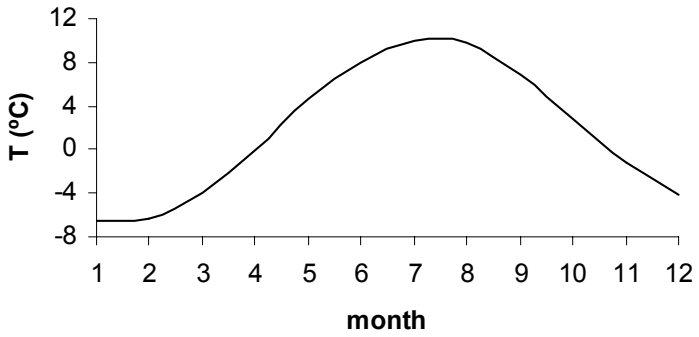


Figure 15. Average temperatures at Skalnaté Pleso (1778m) over the period 1930-1960 (adapted from Mikulaš Konček et al. (Konček, 1974)

3.2.2.4 Human activity

Besides excursionism, alpinism, ski tourism and scientific research, there are no other important activities taking place in the High Tatras. Because of its status as National Park and Biosphere Reserve the High Tatras receive special and strict nature conservation regulations. It is therefor impossible to enter the area by car. There are only two places where the park is accessible by cable cabin. Even the huts situated in the park need to be supplied by manpower, so without use of donkeys or helicopter. This last feature has turned into a tradition among the mountaineers to carry as much load as possible on their backs up to the mountain. The record is held be the owner of the hut Skalnatá Chata, Laco Kulanga, who carried 207.5kg of supply 530m up to the mountain in less than 6 hours. At lower parts of the mountains some forest management is done. The Tatras are further surrounded by relatively small settlements. The largest nearby cities are Zakopane, in the north-west of the mountain range, and Poprad, in the south-east. Both cities are situated at distances of about 50km from the High Tatras. After the Second World War (WWII) the region has remained quite rural. However, in different parts of the former Eastern Germany, Czecho-Slovakia and Poland mining, metallurgical and chemical industry were highly developed. Contamination

effects of emissions from these industries are documented and reflected in the destruction of forests by acid rain and the acidification of the lakes from the Bohemian Forest and Sweden (Kopácek et al., 2002). The effect of atmospheric contamination in the High Tatras is measured in the waters and sediments of its lakes, where very high levels of SO_4^{-2}, NO_3^- and PAH were found (Fernández et al. 1999; 2000; Kopácek et al., 2002).

Table 4. Physical characteristics and water chemistry of the studied lakes

Name		Estany Redon	Dlugi Staw	Starolesnianske Pleso	Ladove Pleso
Geo. Position		42º03´N; 00º46´E	49º13´N; 20º00´E	49º10´N; 20º10´E	49º11´N; 20º09´E
Altitude	(m)	2240	1783	2000	2057
Area catchment	(ha)	155	65	2	13
Area lake surface	(ha)	24	1,6	0,7	1,7
Max. depth	(m)	73	11	4	18
Alk.	(meq/L)	45	22	2	65
PH		6,7	6,2	5,3	6,6
TOC(1	(mg/L)	1,1	0,2	4,2	na(2
TP	(µg/L)	1,0	1,0	8,0	2,0
TN	(µg/L)	220	534	211	276
Cond.	(mS/m)	1,2	1,5	0,9	1,4

Data from EMERGE project 2000; 1) TOC data from MOLAR project; 2) na: not analysed.

Chapter 4 Atmospheric transport and fate of POP in remote mountain areas

Chapter 4. Atmospheric transport and fate of POP in remote mountain areas

The atmosphere is the most important pathway for POP transport to the remote sites (Ballschmiter, 1992; Duce et al., 1991). These compounds have vapour pressures between 10^{-2} and 10^{-5} Pa (see Chapter 2, Table 3) which are in the range of phase changes at the ambient temperature intervals. In this way POP tend to evaporate at ambient temperature rising and condense at temperatures decline. This process has been given many names depending on the phenomenon that was to be explained. "Global Distillation" (Goldberg, 1975), explains processes mimicking a gas chromatograph. Compounds that evaporate faster (less energy needed to change stationary phase for gas phase) will have larger atmospheric mobility than those needing higher temperatures to evaporate and to maintain in the gas phase (4.1). Others have described these processes under names "Global" or "Latitudinal Fractionation", and "Cold Condensation" or "Selective Trapping" (Wania and Mackay, 1993, 1996; Argell et al., 1999; Grimalt et al., 2001). The principle is the same as the distillation process and has been used to explain the change in POP composition in different environmental matrices in relation to latitude (Calamari et al., 1991; Argell et al., 1999; Ockenden et al., 1998; Kalantzi et al., 2001) and altitude (Calamari et al., 1991; Galassi et al., 1997; Blais et al., 1998; Grimalt et al.,2001). "Grasshopping" is used for the process of POP migration in short jumps, depending on the seasonal changes in temperature at mid-latitudes (Figure 16).

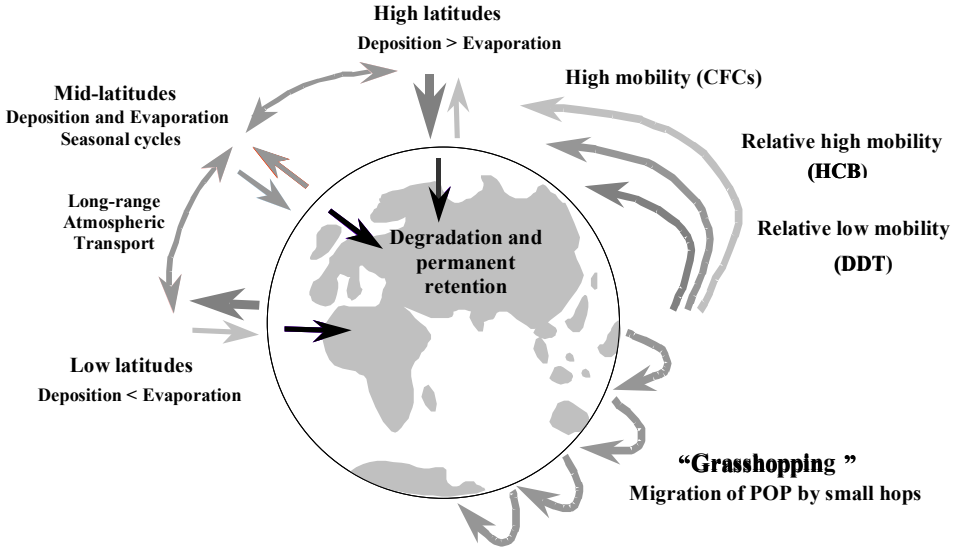


Figure 16. POP migration. Global deposition processes are more significant than evaporation at high latitudes / altitudes and low temperatures (adapted from Wania and Mackay, (1996).

Atmospheric POP appear both in gas and particulate phase. The distribution between the two phases is also temperature dependent (Pankow and Bidleman, 1992). Photo-degradation and deposition are also relevant for the long-range transport of POP (4.2). Once the compounds have deposited on land or superficial water they could be incorporated in these compartments. The retention capacity of soils and lake sediments depend on several factors, such as its organic content, ambient temperatures, biological activity, physical disturbance, chemical transformation, etc. (4.3) (Sanders et al., 1995; Fernández et al., 1999; 2000; Ribes et al., 2002; 2003); Meijer et al., 2003).

4.1 Atmospheric dynamics of POP

The energy needed for POP evaporation/condensation is different for each compound. Table 5 shows the theoretical enthalpies of vaporisation (and condensation) of several organochlorine compounds. The relationship between the vapour pressure and the phase change enthalpies is based on the Gas Law

$$\text{Ln } P = - \Delta H_{vap} / RT + \text{constant} \qquad \text{(Hoff et al., 1998)}$$

where Ln P is the natural logarithm of the partial vapour pressure (atm or Pa), R is the universal gas constant (8,3145 J mol^{-1} K^{-1}) and T the environmental temperature (K)

Table 5. Theoretical phase change enthalpies of vaporisation from a sub-cooled liquid (Hinkley et al., 1990) for OC pesticides, (Kömp and McLachlan, 1997b) for PCBs)

	ΔHvap (kJ/mol)
α-HCH	68
γ-HCH	70
Endosulphanes	95
4,4´-DDE	87
PCB18	75
PCB28	78
PCB52	81
PCB101	85
PCB110	87
PCB149	90
PCB118	91
PCB153	92
PCB138	97
PCB180	97

Vapour pressure can be transformed into gas phase concentration by adequate change of units.

$$\text{Ln [conc POP]} = - \Delta H_{vap*} / RT + \text{constant}$$

where ΔH_{vap*} is the pseudo-enthalpy. In laboratory studies the plots are calculated for systems in equilibrium. True equilibrium between the atmospheric gas phase and a surface in the environment may not always be the case. The slope of the plot resulting from representation of the previous equation should therefor be considered as the pseudo-enthalpy of phase change. Comparing the slopes of environmental and laboratory data may provide information on the processes of vaporisation or condensation of POP in the environment. The steepness of the slopes may be related to the influence of potential sources on the atmospheric samples (Wania et al. 1998). Steep slopes (high temperature dependence, high pseudo-enthalpies) indicate high surface concentrations in the vicinity of the sampling site. Shallow slopes (low temperature dependence, small pseudo-enthalpies) indicate long-range transport.

4.2 Atmospheric removal pathways

Photo-degradation (4.2.1) and deposition (4.2.2) can eliminate and remove POP from the atmosphere. The former process is irreversible and the later may be reversible. These processes are important to estimate the atmospheric POP lifetimes. Taking in consideration all these mechanisms, the capacity of POP to stay in the atmosphere can be estimated.

4.2.1 Photo-degradation

One of the possible removal pathways for atmospheric POP is degradation due to direct or/and indirect solar radiation. In the past, few investigations have been done to study the possible effects on POP. Direct degradation, or primary photo-degradation, indicates photo-reactions light with a chemical, either by absorption or by energy transfer from an excited photo-sensitiser. In the second case, indirect degradation, or secondary photo-degradation, refers to photo-reactions of chemicals with photolytically-generated radicals, for example hydroxyl radicals, ozone, singled oxygen, or a photo-chemically-generated base, which catalyses hydrolysis (Lemaire et al., 1982). So far, no investigation has been performed to study the effect of primary and secondary photo-degradation of POP *in situ*. And only few papers describe experiments under laboratory conditions (Bunce, 1982; Atkinson and Aschmann, 1985; Bunce et al., 1989; Anderson and Hites, 1996a, b; Brubaker and Hites, 1998a, b).

Bunce *et al.* (1982) describes primary and secondary photo-degradation of PCBs in liquids and solids as test media and/or light sources with wavelengths less than 295nm and under high temperatures. These conditions are not found in the environment. However, laboratory experiments using a wavelength 250nm show that the ortho-substituted chloro atoms in the biphenyl molecule have the highest excited-state energies. Furthermore, this study shows that PCBs can be photo-oxidated by direct solar light, even at wavelengths < 300nm (in liquid system). Later Bunce *et al.* (1989) calculated lifetimes for 2-, en 4-chlorobiphenyls (one chlorine substitution) of

less than one week, in an experimental model at wavelengths from 295 – 345nm For 3-chlorobiphenyls (one chlorine substitution) lifetimes of more than one week were calculated. Atkinson *et al.* (1985) and Atkinson (1987) calculated lifetimes of ≈8, ≈4, and ≈6 days for respectively 2-, 3-, and 4-chlorobiphenyl after direct photolysis. For higher chlorinated biphenyls the average lifetimes range from a few weeks for dichlorobiphenyls (2 Cl substitutions = 2CB) up to a few months for pentachlorobiphenyls (5 Cl substitutions = 5CB)

OH radical attack is probably the most important photo-degradation pathway for POP in the atmospheric gas phase. This process can modify the levels and the composition of POP in air masses during long-range atmospheric transport. It is however very difficult to measure this process since both POP and OH concentrations should be analysed *in situ* following an atmospheric transact. This air mass should not have any interaction with surfaces or other air masses. Furthermore, both POP and OH levels are very low and OH-radicals have extremely short atmospheric lifetimes (10^{-3} seconds), which is complicating even more their analysis.

Anderson and Hites (1996a, b) described a method of PCB degradation by OH-radicals. OH radicals were generated by the reaction of O_3 and UV light ($\lambda < 320$nm) and water vapour inside a crystal chamber that was connected to a MS. Injection of cyclohexane and 4,4´-dichlorobiphenyl (2CB) and higher chlorinated biphenyls, up to penta-CB (5 Cl substitutes = 5CB), into this chamber allowed to calculate the degradation of PCB by OH using toluene to calibrate the system. In order to obtain PCBs in the vapour phase, the experiments were done at a temperature range between 323K and 363K (50ºC – 90ºC). The temperature dependence of the reaction rates was studied within this interval.

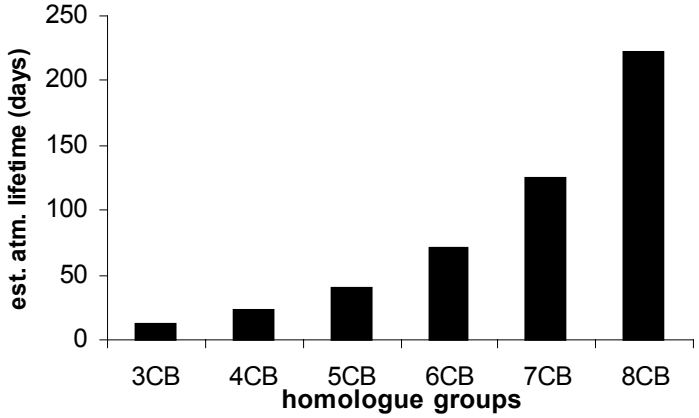


Figure 17. Estimated atmospheric lifetimes of PCB homologue groups due to reaction with OH. Lifetimes calculated based on 24-h global average OH concentration of 8.8 x 10^5 cm^{-3} and kOH at 0ºC (0-4km altitude) (adapted from Anderson and Hites, (1996b) and Spivakovsky et al., (2000).

Unfortunately, the temperature interval was not representative of ambient temperatures (213K and 313K = -60ºC and 40ºC). The same problem occurred with the concentrations of OH radicals and PCBs in the reaction chamber. OH radical concentrations were around 10^9 molecules cm^{-3}, while average ambient concentrations are around 10^6 molecules cm^{-3} (Spivakovsky et al., 2000). PCB concentrations in the experiments were around 10^{14} molecules cm^{-3}, while ambient concentrations are around 10^4 molecules cm^{-3}. In the case of OH radicals there is a difference of 3 orders of magnitude, while in the case of PCBs the differences are about 10 orders of magnitude. Although reaction rates are *a priori* concentration independent, the very high OH and PCB concentrations may cause a situation where there is never a shortage of compounds to undergo the reaction, and thus result in high reaction rates. In contrast, the much lower tropospheric concentrations of the compounds may result in a shortage of one of the compounds for reaction and a reduction of the PCB-OH reaction rates.

The observed temperature dependence was used to extrapolate the reaction rates and atmospheric lifetimes under environmental conditions (first 4km of the troposphere (273K)) for 4,4'-dichlorobiphenyl and higher chlorinated PCBs (Figure 17). For PCBs it seems that higher chlorination slows down the reaction rate, thus increases the atmospheric lifetime. For tri-, tetra- and pentachlorobiphenyls (3CB, 4CB and 5CB) atmospheric lifetimes of 13, 23 and 40 days were estimated, respectively. Anderson and Hites (1996b) only calculated atmospheric lifetimes until pentachlorobiphenyls (PCB#95, #110 and #116). The atmospheric lifetimes for higher chlorinated PCBs can be estimated by extrapolation of the reaction rates of the different homologue groups. These extrapolations give rise to atmospheric lifetimes for hexa-CB, hepta-CB and octa-CB (6CB, 7CB and 8CB) of 71, 125 and 222 days. Although the results obtained are in agreement with the structure-activity tests of Atkinson *et al.*(1985) and Atkinson (1987) one should be cautious upon application of the reaction rates for quantitative calculation of environmental data. However, they may give a good qualitative indication of the atmospheric transformation of PCB. Similar experiments, as done by Anderson and Hites (1996b), were performed by Brubaker and Hites (1998a, b) for HCHs, HCB and PAHs. Atmospheric lifetimes of 120, 96 and 940 days for α-HCH, γ-HCH and HCB, respectively, and 22, 11, 1.5, 26 days for fluorene, phenanthrene, anthracene, and pyrene, respectively, were observed.

4.2.2 Deposition

POP deposition takes place by: 1) snow and rain scavenging of gasses and aerosols (wet deposition), 2) dry particulate deposition and 3) gas exchange with surfaces (Cotham and Bidleman, 1991). POP can occur both in gaseous and particulate phase (aerosols), which depends on the affinity of each compound for a certain particle as well as atmospheric temperature, particle amounts, and particle composition (Pankow, 1987; Pankow and Bidleman, 1992).

4.2.2.1 Wet deposition

Wet deposition involves the transfer of gasses and aerosols to ground surfaces by rain, snowfall, etc. Water solubility and vapour pressure of POP are very important in these processes. If a compound is more water-soluble it will be washed out faster from the atmosphere. The ratio between vapour pressure to the water solubility defines the Henry´s Law Constant (H). H-values are used in the calculations for the wash out of gaseous compounds (W_g), and thus the efficiency in which rain (C_{rain}) or snow removes a gaseous compound from the atmosphere ($C_{air\ gas}$) (Cotham and Bidleman, 1991):

$$W_g = C_{rain} / C_{air\ gas} = RT / H \qquad \text{(mass/volume)}$$

This equation shows that compounds with low H tend to be washed out faster than compounds with high H.

The wash out factor for the particulate phase (W_p) is important for rain and snow scavenging of particle-bounded POP ($C_{air\ particulate}$) (Cotham and Bidleman, 1991).

$$W_p = C_{rain} / C_{air\ part} \qquad \text{(mass/volume)}$$

However, W_p is very variable and depends, for example, on the size of the particle, its structure and chemical composition, and meteorological conditions.

4.2.2.2 Dry deposition

The dry deposition velocity of particles and particulate-bounded compounds depends largely on the size and composition of the aerosol. For large particles (>25μm) gravity is mainly governing the deposition and aerosols are deposited near the emission source. Smaller aerosols, particle sizes between 0.1 and 10μm, are able to make long atmospheric journeys over more than hundreds of kilometres. Invasions of Saharan dust to the North Atlantic and Europe mainly consist of aerosols of these sizes. Particles smaller than 0.1μm depend on molecular diffusion (Cotham and Bidleman, 1991). POP have higher affinity to particles with high then low organic carbon content, due to their relative high lipophility ($\log K_{ow}$ >4).

Particulate flux to a surface ($F_{d\ part}$) and the particle-bounded atmospheric concentration of a compound ($C_{air\ part}$) at a given height are related through the dry deposition velocity ($V_{d\ part}$).

$$V_{d\ part} = F_{d\ part} / C_{air\ part} \qquad \text{(mass/area·time)}$$

This velocity is very variable and depends on the meteorological conditions, particle size, composition and surface properties.

The adsorption onto soot-carbon (SC) has been shown to affect significantly the overall PAH sorption to certain aerosols (Gustafsson et al., 2001; Bucheli and Gustafsson, 2000; Dachs and Einsenreich, 2000) and is held to be the principal factor of transport of atmospheric particle-bounded PAH to European high-mountain areas (Fernández et al., 2002).

Analysis of wet (rain and snow) and dry deposition annual fluxes in European high-mountain areas have shown that the lighter and lower molecular weights compounds are in general more abundant than the heavier compounds. These lighter compounds occur predominantly in the atmospheric gas phase, while the heavier compounds are essentially particle-bounded (Pankow and Bidleman, 1992). The transfer mechanism of gas phase POP to rain and/or snowflakes is very effective (Carrera et al., 2001; 2002). Thus, wet deposition is accounted to be the predominant pathway of gas phase and particulate phase POP to these mountain areas. The overall transport depends on the quantity of precipitation, which shows high variability between different sites and seasons (Carrera et al., 2001; 2002; Fernández et al., 2003). Although higher PAH levels are observed in the colder season (winter), due to increasing combustion of fossil fuels and reduced photooxidation rates, warmer periods (spring and summer) show highest atmospheric PAH deposition, probably due to high precipitation in these seasons as compares with winter (Fernández et al., 2003). Higher OC deposition is also related to the wet seasons (Carrera et al., 2002).

4.2.2.3 Gas exchange

The exchange of chemical compounds between the gas phase and ground surfaces (soil, water, vegetation) is controlled by the tendency of the compound to be absorbed/adsorbed by these surfaces The ratio of vapour pressure to water solubility can be used as indicator between levels in the atmosphere and water surface. The ratio between POP levels in octanol and water is used as estimate for the distribution of POP in organic material, giving the octanol-water partitioning coefficient (K_{ow}) (Mackay et al., 1992). Consequently, from H/RT (C_{air})/C_{water}) and K_{ow} ($C_{octanol}$/C_{water}) one can obtain the octanol-air partitioning coefficient (K_{oa}),

$$K_{oa} = K_{ow}\, RT / H$$

which can be used as the indicator for the distribution of POP between the atmosphere and (organic) surface (Kömp and McLachlan, 1997a). Since H is temperature dependent, K_{oa} is temperature dependent as well (Kömp and McLachlan, 1997b). Thus, there can be a flux from the air to the surface (surface is sink), or from the surface to the atmosphere (surface is source). This exchange is complex and depends on many factors, like, properties of compound, meteorological conditions, especially temperature, surface area, and thickness of boundary layers between environmental compartments.

Vegetation has been used in the past as indicator for atmospheric contamination on small and global scale (Calamari et al., 1991; Simonich and Hites, 1995; Kömp and McLachlan, 1997a).

Although there are important differences between species, in general the lipophilic organic pollutants ($logK_{ow} > 4$) are exclusively taken up from the atmosphere via the cuticle waxes or by the stomata of the leaf, where they tend to accumulate in the leaf. Uptake of these compounds from the soil via the roots is not significant, neither are POP transported to other parts of the plant. Due to the large surface area of leaves, atmospheric variability of POP levels and ambient temperatures affect directly the concentrations found in the leaves of plant species (Simonich et al., 1995). In remote sites leaves can therefore be useful as bio-indicators POP levels, since they are easily collected and most POP have $logK_{ow} > 4$.

4.2.3 Atmospheric persistence and long-range transport

As mentioned before, the atmospheric behaviour of POP is mainly controlled by the physical conditions of the atmosphere and the physico-chemical properties of the compounds. Atmospheric lifetime is used to study the air persistence of the compounds and their feasibilty to undergo long-range transport. Gramatica *et al.* (2001) modelled the atmospheric half-lives of 12 POP and 48 additional compounds that could be POP, using different molecule structure descriptors in a regression QSAR (Quantitative Structure-Activity Relationships) model. In these QSAR models the environmental chemical properties were calculated by combination of the molecular structures and physico-chemical properties of the compound with environmental conditions using several statistical tests (PCAs). Indices for atmospheric persistence and long-range transport were obtained (Table 6). These indices may be useful for a first evaluation of the atmospheric mobility of POP. Other models are based on fugacity calculations (Mackay et al., 1992; Beyer et al., 2000).

Table 6. Atmospheric half lives of some POP (adapted from Gramatica *et al.*, (2001)

Name	Atmospheric half life values (h)	
	Average	maximum
Fluorene	37,2	67,6
Anthracene	1,1	1,7
Phenanthrene	11,0	20,0
Fluoranthene	11,2	20,4
Pyrene	1,3	2,0
Chrysene	4,4	7,9
Benz[a]anthracene	2,0	3,0
Benzo[b]fluoranthene	7,9	14,5
Benzo[a]pyrene	0,7	1,1
Benzo[ghi]perylene	1,8	3,2
Dibenz[ah]anthracene	2,3	4,3
PCB18	525	724
PCB28	586	724
PCB52	1023	1445
PCB101	2138	2884
α-HCH	51	93
γ-HCH	51	93
HCB	20417	37154
4,4´-DDT	98	178
4,4´-DDE	98	178

The atmospheric half-lives PAH may be hours or days. Those of organochlorine pesticides, α-HCH, γ-HCH, *4,4´*-DDE and *4,4´*-DDT, of days or weeks, and PCBs of weeks or months. HCB has the largest atmospheric half-life encompassing a few years (Table 6).

The atmospheric half-lives of PCBs are somewhat higher than the residence times estimated from OH radical reactions of Anderson and Hites (1996b). Recently the atmospheric degradation of PCBs by OH radicals has been evaluated (Axelman and Gustafsson, 2002). Application of the reaction rates as observed by Anderson and Hites (1996b) on environmental data would result in one order of magnitude faster depletion of the less chlorinated PCBs (more reactive) in comparison to the more chlorinated PCBs (less reactive). However, there are no temporal and spatial trends observed in environmental samples that give evidence for an such enhanced depletion of less chlorinated PCBs. For example, the composition of PCB congeners is more or less the same along historical samples, such as sediment cores (Sanders et al., 1995). Moreover, the estimated quantity of degraded PCBs is of such an amount that it would outnumber the loss of PCBs from the environment by other processes, such as sink to oceanic sediments. Even in a scenario of maximum annual PCB emissions (Breivik et al., 2002) this would not be enough, by orders of magnitude, to compensate for the annual loss of PCBs by OH radical reactions. As mentioned before, the experimental conditions under which the PCB-OH reaction rate constants were obtained may be to far from the environmental conditions. Application of these rate constants may lead to an overestimation of the atmospheric loss of PCBs, especially on the more volatile and reactive congeners.

The work of Junge (1974) can be used as an alternative to estimate the atmospheric residence times of chemical compounds. Studying a large set of field data from different trace gasses provides an empirical relationship between the tropospheric residence time (τ_{total} (year)) and the tropospheric variability in concentrations. This relation is described as:

$$\tau_{total} = 0.14 / RSD_{total}$$

where RSD_{total} is the total variability observed in the concentrations expressed as a relative standard deviation (standard deviation divided by mean concentrations). The inverse of the residence time is a compilation of the different processes involved in the loss of compounds from the troposphere, such as degradation and deposition. The tropospheric residence time can therefore be described as:

$$1/\tau_{total} = 1/\tau_{react} + 1/\tau_{dry\ dep} + 1/\tau_{wet\ dep}$$

where τ_{react} is the residence time due to chemical reactions, $\tau_{dry\ dep}$ is the residence time due to dry deposition and $\tau_{wet\ dep}$ is the residence time due to wet deposition. Each of these processes also includes several other processes. However, τ_{react} is here assumed to be τ_{OH}; the residence time due

to reactions with OH radicals. If τ_{OH} is longer than τ_{total} there should be other loss processes more important than the reaction with OH radicals. If τ_{OH} is shorter than τ_{total} then one of the estimates is wrong (Axelman and Gustafsson, 2002).

Values for τ_{total} were calculated from year round atmospheric samples collected at remote sites on the Northern and Southern Hemisphere (see Results. Global-Soc database). For the less chlorinated CBs (3CB, 4CB and 5CB) τ_{OH} is shorter than τ_{total}, while τ_{OH} for the more chlorinated CBs (6CB and 7CB, and probably 8CB) is longer than τ_{total} (Figure 18). This indicates that for the more chlorinated PCB other loss processes, like deposition, are more important than OH radical reaction. The fact that the less chlorinated PCB show slightly higher τ_{total} than the more chlorinated PCB shows that the tropospheric variability is not under influence of OH radical reaction, since these reactions would evidence shorter residence times for these compounds. Alternatively, residence times calculated by the Junge equation could be over-estimated.

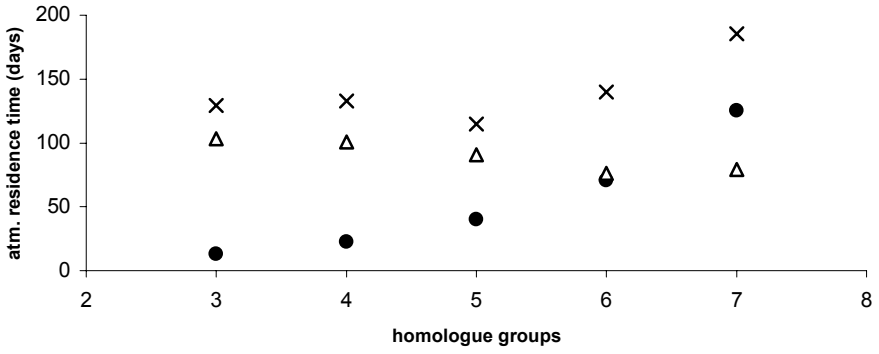


Figure 18. Residence times (in days) of τ_{OH} (black dots), τ_{total} (triangles) and τ_{real} (stars) for the different homologue groups of PCBs.

The atmospheric samples are collected with HiVol samplers and analysed in laboratories. During sample handling and analytical procedures several steps could add an error to the observed variability. This variability could be called ´sample+analysis´ variability. Although, no value exists for the collected samples an attempt was made to obtain the ´$\tau_{sample+analysis}$´. In this case, one sample was injected four times during one year and analysed on PCB congeners. The obtained relative standard deviation range from 0.1 to 0.3 for the different PCB congeners, which is consistent with the 0.1 from Oehme et al. (1996). The real residence time (τ_{real}) is expressed as:

$$\tau_{real} = 1/\tau_{total} - 1/\text{´}\tau_{sample+analysis}\text{´} \qquad \text{(Axelman and Gustafsson, 2002)}$$

Applying this ´correction´ to the total residence time, figure 18 shows that τ_{OH} is even further separated from the residence times based on the Junge model. Now, less chlorinated PCBs (3CB,

4CB and 5CB) have similar or slightly lower residence times than the more chlorinated PCB (6CB and 7CB, and probably 8CB). These results might indicate that the OH reactions have influence on the less chlorinated PCBs but that the reaction rates are not the ones calculated by Anderson and Hites (1996b). Application of the Junge model to estimate the tropospheric residence time of PCBs does not allow to elucidate which fraction is removed irreversibly from the troposphere (photo-degradation) and which fraction is removed reversibly (deposition). Deposited PCB could re-volatilise and form part again of the troposphere. Application of the Anderson and Hites (1996b) reaction rates may indicate which is the loss of PCBs from the troposphere, however, the very high PCB loss is not realistic in comparison to other loss process and emission data. Moreover, there are no evidences in environmental data that such a depletion takes place. One way or another, the findings suggest that there is still a wide gap of knowledge in the understanding of the atmospheric fate of these compounds.

4.3 Retention of POP in soils and sediments

On a global scale only a small percentage of soils and sediments receive POP from direct input. In the case of most POP these soils are situated on the Northern Hemisphere between 30º - 60ºN. Remote background soils, for example, occupy more than 99% of the total soil surface. These are soils where POP are deposited after long-range atmospheric transport and where atmosphere and soil surface are in certain state of equilibrium (Meijer et al., 2003). When POP are deposited on water surfaces sedimentation processes can take place and particle-bounded POP can be incorporated into sediments. Although many factors influence soil and sediment retention capacity for POP, in general, both compartments act as significant sinks for these compounds in remote areas (Fernández et al. 1999; 2000; Ribes et al., 2002; Meijer et al., 2003). In the past few years, accumulation of POP in soils and sediments have been used to reconstruct the historical input of these compounds to source and remote areas (Sanders et al., 1994; Fernández et al., 2000).

4.3.1 POP in remote soils

Soils can be used as spatial and temporal indicators for the atmospheric levels and deposition levels of POP (Sanders et al., 1995; Meijer et al., 2003). As mentioned before (4.2.2.3) the exchange between the atmosphere and surface, which could be soil, is depending on the concentrations in the both compartments as well as the properties of the compound, the soil and the atmosphere. Factors which *a priori* favour the POP transfer from atmosphere to soil, or the POP retention in soil, are relatively high air POP concentrations, low ambient temperatures, low soil POP concentrations and high soil organic carbon content (Fernández et al, 2000; Ribes et al, 2002; Meijer et al, 2003). Low ambient temperatures and high organic carbon content have also influence on the POP sorption in soils. Soil samples collected on the Island on Tenerife at 26 altitudes between 10m and 3400m have shown a very good positive correlation between OC levels

and the organic matter in the soils. Moreover, the concentration of most of the analysed OC increased with altitude, so when temperatures decrease (Ribes et al, 2002). The partitioning of POP between soil and air can be expressed as

$K_p = C_{soil} / C_{air}$ (volume / mass)

where K_p is the soil-air partitioning coefficient and C_{soil} the POP concentration in soil (mass / mass) and C_{air} the POP concentrations in the atmospheric gas phase (mass / volume).

Prediction of POP partitioning between the soil and atmosphere can be done using the octanol-air patitioning coefficient (K_{oa}). As mentioned in 4.2.2.3. this coefficient is temperature dependent. Further on, the soil organic content and the properties of the organic matter have also to be considered (Finizio et al, 1997; Harner et al, 2001). The partitioning of POP between soil and atmosphere can be expressed as

$$K_p = f_{OM} (\xi_{OCT} / \xi_{OM})(MW_{OCT}/MW_{OM}\, \delta_{OCT})\, K_{oa}$$

where f_{OM} is the fraction of organic matter in soil, and ξ_{OCT} and ξ_{OM} are the activity coefficients of the individual POP in octanol and organic matter, respectively. MW_{OCT} and MW_{OM} are the molecular weights of octanol and organic matter, respectively, and δ_{OCT} is the octanol density (0.820 kg L^{-1}; at 20ºC). After the assumptions that

$$f_{OM} = 1.5\, f_{TOC}$$
$$(\xi_{OCT} / \xi_{OM})(MW_{OCT}/MW_{OM}) = 1$$

where f_{TOC} is the fraction of total organic carbon in the soil, the K_p is given by

$$K_p = 1.5\, (f_{TOC}/\delta_{OCT})\, K_{oa}$$

This adsorption model requires only knowledge on two easily measurable parameters, K_{oa} and f_{TOC}.

However, besides temperature and organic matter, POP retention in soils could additionally influenced by processes, such as biodegradation, formation of non-extractable residues, and transfer to depths. The last process can both take place by bioturbation as well as by infiltration of precipitation (Meijer et al, 2003). In soils of the high-mountain areas biological activity is slow, due to low temperatures, thus it can be assumed that biodegradation and bioturbation will be of small influence for POP retention in these soils.

4.3.2 POP in remote lake water and sediments

Lake sediments of remote high-mountain areas can be considered as archives of lake response to anthropogenic pollution and climate changes (Guilizonni et al, 1998; Kameniket al, 2000; Fernández et al, 2000). They include mineral particles and dissolved ions from run-off from the lake catchment and atmospheric deposition. Further more, there is a fraction of biogenic inorganic material, including diatoms frustules, remains of zooplankton and benthic organisms, and calcium carbonates (Guilizonni et al, 1998). The organic fraction consists of resistant substances of vegetal and animal origin, like pigments, pollen, etc., but they can also contain significant amounts of POP from atmospheric deposition.

The input of POP to the lake is directly related to atmospheric deposition. Depending on the physico-chemical properties of the compound and the physical conditions of the atmosphere, the compounds may enter the lake dissolved in rain drops, absorbed or adsorbed in/to particles and snow flakes, and dissolved or particle-bounded in the run-off from the lake catchment after rainfall or snowmelt (see 4.3.3). Once POP have entered the lake new interactions may take place between the compounds and particles in the lake waters. This depends on their water solubility, or their affinity to organic material, as well as on the physical conditions, like the temperature, in the water column (Karickhof et al, 1979; Chiou et al, 1983; Mackay and Powers, 1987; Baker et al., 1991; Swackhamer and Skoglund, 1993). The POP with relatively high solubility, like the HCHs, are present in the dissolved phase, while PCB and PAH are in general more related to the particles in the water column (Vilanova et al., 2001a, b, c). Although atmospheric POP levels in different European high-mountain lakes are lower than in lakes at lower altitude, relatively high concentrations of γ-HCH and endosulphanes are detected in Estany Redon (Central Pyrenees) in springtime (Vilanova et al., 2001c). Their occurrence is related to the application of these products for agricultural purposes in the European continent. Other OC show a relative constant distribution round the year. Uniform POP distributions are observed in the water column once they have entered to lake waters. Part of the dissolved POP may be absorbed actively or passively by zooplankton and phytoplankton species, or by higher organisms, such as fish, via ingestion, respiration, and diffuse absorption (Vives et al. 2004). Further on, fish have the ability to ingest particles and zoo/phytoplankton species from the water column or sediments (Varanasi, 1989; Baumard et al.,1998). Inside organisms some compounds will accumulate in body tissue, while others will be transformed to other compounds by metabolisation or excreted in its original form (Barron, 1990; Clark et al., 1990, Gobas et al., 1993; Spacie et al., 1995).

The degree of contamination of the aquatic system can be assessed by comparing the concentrations of pollutants in young sediments (top layer) with values in older (deeper) sediments. The average level in the later can be used as baseline value for the lake system. Analysis of a certain section of the sediment could evaluate not only the degree of contamination but also the temporal trend. In this case the chronology of the core is necessary. This is normally estimated from the

changes in concentrations of natural radioactivity. The natural fallout of lead-210 (^{210}Pb) can be used for these purposes. ^{210}Pb is produced at a steady rate by decay of radon gas (^{222}Rn) in the atmosphere. Attached to particles ^{210}Pb is deposited on the lake surface and further transported through the water column to form part of the sediment. The buried ^{210}Pb undergoes radioactive decay with a half-life of 22.3 years. When sediments are collected and the ^{210}Pb concentration is measured, it is possible to calculate the time span at which each layer was buried. ^{137}Cs and ^{241}Am can also be used for dating as implementary tools. They are consequence of the weapon fallout and nuclear power accidents, such as Chernobyl (1986) (Appleby and Oldfiled, 1978; Appleby, 2001).

4.4 Environmental fate of POP in remote high altitude areas

Figure 19 shows a graphical summary of the transport and fate of POP to high-mountain areas in general and specifically lakes, based on the information presented in the former paragraphs. Due to the lack of local sources POP enter the high-mountain ecosystems after long-range atmospheric transport. During this transport some degree of photo-oxidation could take place for certain compounds, which influences the levels and composition of the POP. Once they are deposited they can become part of the soils, lake waters, organisms and eventually lake sediments. The principal factors responsible for the presence of POP in these areas are semi-volability, resistance against degradation, and the ambient temperatures.

One can conclude that the remote high altitude areas constitute an ideal system for the analysis of long-range atmospherically transported POP, because

1) atmospheric transport is the only input,
2) long residence times of POP in these oligothropic systems,
3) retention of certain POP because of low temperatures,
4) slow sedimentation rate in these lakes because of low primary production,
5) low biodegradation in soils, lake waters and sediment because of low temperatures,

These characteristics have favoured the concentration of POP in thin soil or sediment layers. Further more, the low ambient temperatures enhance their accumulation. This results in concentration rather than dilution effects of certain POP after long-range atmospheric transport to these areas (Blais et al., 1998; Fernández et al., 2000; Grimalt et al., 2001). More over, since lower ambient temperatures are related to higher altitudes increases are observed for the concentration of certain organochlorine compounds with increasing altitude (Blais et al., 1998; Grimalt et al., 2001).

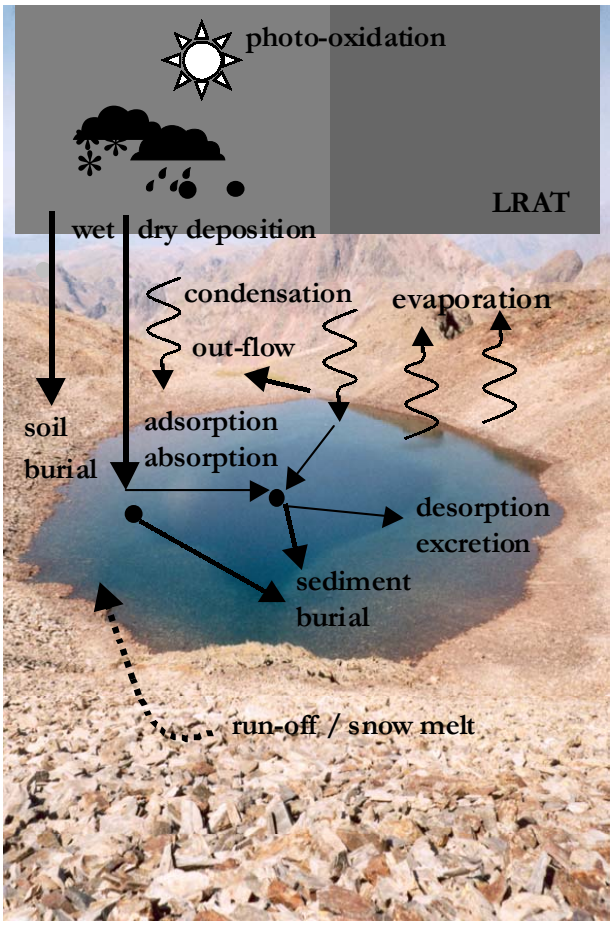


Figure 19. Atmospheric transport and fate of POP in remote high-altitude mountainous areas

Chapter 5 Methods and Materials

Chapter 5. Methods and Materials

5.1 Atmosphere

Between June 1999 and January 2003 atmospheric samples were collected for POP analysis on the Island of Tenerife (June 1999 – July 2000), the Central Pyrenees (November 2000 – January 2003), and the High Tatras (June 2001 – June 2002). The sampling method was the same for all these sites. In the case of Tenerife and High Tatras the collected samples were sent to the analytical laboratory in Barcelona by aeroplane, while in the case of the Central Pyrenees the samples were transported by car to the same laboratory. The general sampling and analytical method are presented in 5.1.1. Paragraph 5.1.2 and 5.1.3 deal with the back-trajectories and temperature determination, respectively. This additional data is used for the interpretation of atmospheric data in terms of origin of sampled air masses and temperature dependence. Atmospheric deposition samples have been collected on the Island of Tenerife between June 1999 and June 2000. The sampling and analytical methods are presented in 5.1.4. Identification and quantification of the analysed POP in the extracts are presented in 5.1.5.

Figure 20. HiVol-sampler for atmospheric gas and particulate sampling on the border of Estany Redon.

Figure 21. Deposition sampler at the Atmospheric Observatory of Izaña. On the background the peak of Teide is visible (Foto: Sandra Ribes)

5.1.1 Atmospheric gas and particulate phase

Air was collected with a high volume (HiVol-) sampler (MCV S.A., Collbato, Catalonia, Spain) (Figure 20). POP in the gas phase were extracted from the air matrix with two polyurethane foam (PUF) plugs (diameter 6 cm; height 10 cm; density 28.5 kg/m^3) packed inside a Teflon© tube. Glass fibre filters (GFF; type GF/B; 20.3 x 25.4 cm; 1.6 μm pore size; Whatman International Ltd., Maidstone, England) were used to collect the particulate phase. Before sampling PUFs were Soxhlet extracted with *n*-hexane (Merck, Darmstadt, Germany) for 48 hours. GFFs were cleaned by ashing at 400ºC for 24 hours. PUFs were packed into the Teflon© tubes which were subsequently wrapped in aluminium foil and introduced to heat sealable polyester bags (Kapak corporation, Minneapolis, USA) and stored at –20ºC before transport to sampling sites. GFFs were also wrapped in aluminium foil and introduced into the heat sealable polyester bags and stored at –20ºC before transport. Storage had a durance of about 2 days then PUFs and GFFs were transported to sampling sites below 0ºC in a coolbox containing dry ice. Transport to Tenerife and High Tatras took approximately 2 days.

At the Island of Tenerife and the High Tatras the HiVol-sampler was energy supplied by the electric circuit of the meteorological stations, while at Estany Redon a power generator was used. This generator was always situated upwind from the HiVol-sampler at a minimum distance of 50m. In the Central Pyrenees and High Tatras the HiVol-sampler was installed at ground level where it sampled air at 1.5m height. At Tenerife the sampler was installed on a 15m high tower, in the case of Izaña, and on a 40m high lighthouse, in the case of Punta de Hidalgo. Collected sample volumes were between 80 m^3 and 280 m^3. Every sampling period had one field blank for PUFs and GFFs. The field blanks were also introduced but without running the pump. After sampling the PUFs and GFFs were wrapped in aluminium foils and stored in heat sealable polyester bags, placed inside a coolbox and transported below 0ºC to the laboratory in Barcelona.

Injection of PCB#30 and PCB#209 *in situ* to the samples and blanks after sampling did not show significant losses during transport (recoveries >81%). After this, the surrogates were added to samples and blank in the laboratory. PCB#30 and PCB#209 were added as internal standards for OC analysis and anthracene-d_{10} and benzo(ghi)perylene-d_{10} for PAH analysis. The recoveries of these compounds were used to correct for losses during transport and analysis. Table 7 shows the average recoveries for the gas and particulate phase.

PUFs and GFFs were Soxhlet extracted for 24 hours in 250 mL n-hexane and in 250 mL hexane:dichloromethane (DCM) (Merck, Darmstadt, Germany) (4:1 v/v), respectively. The extracts were vacuum evaporated until 1 mL. Samples and blanks were cleaned-up by adsorption on 2 g of aluminium oxide (Fluka Type 507C, Fluxa AG, Switzerland) and elution with 8 mL of hexane:DCM (9:1 v/v) and 7 mL of hexane:DCM (1:2 v/v). The 1st fraction contained most of the OC (HCB, PCBs, DDTs), while the 2nd fraction contained the PAH, HCHs and endosulphanes. The collected fractions were vacuum evaporated to 1 mL and to near dryness under a gentle stream of nitrogen.

Finally, they were re-dissolved in iso-octane (Merck, Darmstadt, Germany) to 50 μL and stored at –20ºC before injection in a gas-chromatograph.

5.1.2 Back-trajectories of air masses

The origins of the sampled air masses at Tenerife (Izaña and Punta de Hidalgo), Central Pyrenees (Estany Redon), and High Tatras (Skalnaté Pleso) were calculated from back-trajectories using the HIRLAM model (High Resolution Limited Area Model) of the Spanish National Institute of Meteorology (INM). This model is based on isentropic surfaces that provide a more realistic representation than those elaborated from isobaric surfaces (Danielsen, 1961; Merrill et al., 1986). The calculations were performed at 00:00 UTC and 12:00 UTC for five days (5-D) back with one hour step. The isentropic surfaces for each back-trajectory at the atmospheric sampling sites were selected according to the observed potential temperature at the altitudes of the sites. The calculations of back-trajectories were done by Carlos J. Torres-Garcia (Atmospheric Observatory of Izaña, INM, Tenerife, Spain)

5.1.3 Atmospheric temperatures (T_a)

The T_a for the atmospheric sampling periods on Tenerife were obtained from the records of the Atmospheric Observatory of Izaña of the INM. For the Central Pyrenees T_a were obtained from the records the automatic weather station (AWS) situated at the border of Estany Redon and at the Centre of High Mountain Research (CRAM; 1600m). At Estany Redon, T_a were calculated from measurements taken every 30 min. At CRAM, T_a were calculated from the minimum and maximum daily temperatures. In the High Tatras at Skalnaté Pleso the mean atmospheric temperatures for each sampling period were obtained from the registers of the Slovakian Meteorological Institute (SAV) which has a meteorological station at sampling site.

5.1.4 Atmospheric deposition

From June 1999 until June 2000 deposition samples were collected at Izaña on top of a 15m tower. They were collected in stainless steel reservoirs (∅ = 24 cm, A = 452,4 cm^2) using a Model ARS 1010 sampler (MTX, Italy) (Figure 21). Each sampling period encompassed approximately two weeks. After this time the reservoirs were carefully rinsed with Milli-Q water in three successive steps and the rinses were collected together. Blanks were taken before each sampling. Both samples and blanks were filtered with pre-weighted glass microfibre filters (GFF) (Whatman, Maidstone, England (4,7 cm)). These filters were previously cleaned by ashing at 400ºC for 24 hours. After filtration the dissolved phase was extracted using Empore extraction C-18 disks (3M Empore, Harbor City, USA). Vacuum was used to increase the speed of filtration/extraction. PCB congeners #30 and #209 were introduced in both GFF and C-18 disks as internal standards before sample introduction. Then, the GFFs and C-18 disks were wrapped in aluminium foil,

placed in polyester bags and stored at -20°C. These bags were introduced in a coolbox for air transport to Barcelona (approximately 2 days) where they were kept at 0°C.

In the laboratory the C-18 disks were successively extracted with methanol, cyclohexane and dichloromethane (5 mL each) (Merck, Darmstadt, Germany). Sample handling is described in detail elsewhere (Carrera *et al.*, 1998). GFFs were Soxhlet extracted for 24 hours in 100 mL of hexane:DCM (4:1 v/v), respectively. This extract was vacuum evaporated to 1 mL. All samples and blanks were cleaned up with 2 g of alumina and 8 mL of hexane:DCM (9:1 v/v) and 7 mL DCM:hexane (2:1 v/v). The collected volume was vacuum evaporated to 1 mL and further concentrated to 50 μl in isooctane (Merck, Darmstadt, Germany) under a gentle stream of nitrogen. Then extracts were stored at –20ºC before injection to a gas-chromatograph for quantification.

5.1.5 Quantification of atmospheric samples

5.1.5.1 Identification and quantification of OC

Before instrumental analysis tetrachloronaphthalene was added to the vials for correction of possible instabilities. The extracts were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD, Hewlett Packard 5890 Series II). A 50 m fused silica capillary column (0.25mm i.d, 0.25μm film thickness) coated with 5% phenyl 95% methylpolysiloxane (DB-5, J&W Scientific, Folsom, CA, USA) was used for the analyses of HCB, PCB congeners (#18, #28, #52, #70, #101+90, #110, #149+123, #118, #153, #105+132, #138, #158+160, #180, #199, #194), DDTs (*4,4´*-DDE and *4,4´*-DDT) and for the first identification and quantification of HCH (α-HCH and γ-HCH). The oven temperature program was started at 100°C (holding time 1 min), increased to 150°C at 15°C min^{-1}, followed by heating at 4°C min^{-1} to 240°C (holding time 12 min) and finally increased to 300°C at 4°C min^{-1} (holding time 10 minutes). Injector (split/splitless mode) and detector temperatures were 280°C and 310°C, respectively. Helium and nitrogen were used as carrier (0.33mL min^{-1}) and make-up (60mL min^{-1}) gases, respectively. For the confirmation of the quantified HCHs (α-HCH and γ-HCH) and the analysis of endosulphanes (α-endosulphane and β-endosulphane) the extracts were analysed on a gas chromatograph coupled to a mass spectrometer with negative ion chemical ionisation (GC-MS-NICI). A Fisons MD 800 instrument (quadrupole-detector, THERMO Instruments, Manchester, UK) was used. The instrument was equipped with a capillary column HP5-MS (30m x 0.25mm i.d. x 0.25μm film thickness). Helium was used as carrier gas (1.1mL min^{-1}). The oven temperatures were programmed from 90ºC (1 min) to 120ºC at 15ºC min^{-1} and then to 300ºC at 4ºC min^{-1} with a final holding time of 10 min. Samples were injected in split/splitless mode at 280ºC. In the GC-MS-NICI, ion source and transfer line temperatures were 150ºC and 280ºC, respectively. Ammonia was used as reagent gas. Ion source pressure (currently 1.6 Torr) was adjusted to maximize the perfluorotributhylamine ions (m/z 312,

452, 633, and 671). Ion repeller was 1.5 V. Data were acquired in selected ion monitoring mode with dwell time of 0.06 s and span of 0.10 amu. The ions selected for α-HCH and γ-HCH were m/z 71 and 255, respectively. α-Endosulphane and β-endosulphane were selected with m/z 406 and 272, respectively (Chaler et al., 1998).

The external standard method was used for the identification of the peaks in the chromatograms corresponding to the different retention times of the compounds on the column and to quantify the OC. The compounds in this standard were from Dr. Ehrenstorfer (Ausburg, Germany). The concentration range of the external standards covered the range of compound concentrations found in the samples.

Detection limits (determined as three times the standard deviation of the chromatographic noise near the peaks of the analysed compounds) were 0.04-0.23, 0.03, 0.20, 0.08, 0.12-0.15 and 0.05-0.11 pg m^{-3} for PCBs, HCB, *4,4´*-DDE, *4,4´*-DDT, HCHs and endosulphanes, respectively.

5.1.5.2 Identification and quantification of PAH

The quantitative analyses were carried out by gas chromatography coupled to mass spectrometry. Samples were injected in an Agilent 6890 series chromatograph equipped with a 30m fused capillary column (HP-5MS, 0,25mm x 0.25μm film thickness). The oven temperature program started with 90ºC held for 1 min., then it was heated to 130ºC at 12ºC min^{-1} and to 310ºC at 7ºC min^{-1}. The temperature was kept at 310ºC for 10 minutes. The injector, ion source, quadro pole and transfer line were 280ºC, 200ºC, 150ºC and 280ºC, respectively. Helium was used as carrier gas (0,9 ml s^{-1}). A MS selective detector Agilent 5973 series was operating in selective ion monitoring (SIM) with electron impact (71eV). Dwell time was 50 ms $channel^{-1}$. PAH were selected on the following ions: fluorene (m/z=166), phenanthrene (m/z=178), anthracene (m/z=178), fluoranthene (m/z=202), pyrene (m/z=202), benz(a)anthracene (m/z=228), chrysene+triperylene (m/z=228), benzo(b)fluoranthene (m/z=252), benzo(k)fluoranthene (m/z=252), benzo(e)pyrene (m/z=252), benzo(a)pyrene (m/z=252), indeno(1,2,3-cd)pyrene (m/z=276), dibenz(ah)anthracene (m/z=278), and benzo(ghi)perylene (m/z=276). The quantification was performed by external standard method and corrected for surrogate recoveries of anthracene-d_{10} (m/z=188) and benzo(ghi)perylene-d_{10} (m/z=288), added to the samples and blanks before extraction. The recoveries of the surrogates are presented in Table 7. The compounds in this standard were all from Dr. Ehrenstorfer (Ausburg, Germany). Detection limits range between 100 and 400pg for the individual compounds in the samples.

5.2 *Pinus uncinata* and SPMD

Both *Pinus uncinata* and semi-permeable membrane devices (SPMD) can be considered as passive samplers for atmospheric gas phase, since their surfaces are subject to the exchange of gasses, and thus could be used as monitoring systems for atmospheric contamination. The

principles of the exchange process are explained elsewhere (paragraph 4.2.2.3). In the following paragraphs some specific characteristics of the samplers are indicated as well as some aspects of the exchange mechanism of atmospheric OC. Sampling of the leaves of *Pinus uncinata* is presented in 5.2.1 and the SPMD sampling and analytical method is presented in 5.2.2. Identification and quantification methods for the analysis of OC will be presented in paragraph 5.2.3.

Figure 22. *Pinus uncinata* is the uppermost growing tree in the Central Pyrenees. The presented specimen is growing at 2250m near Estany Redon.

5.2.1 *Pinus uncinata*

PCB have high octanol/water partitioning coefficients ($\log K_{ow} > 4$) and show affinity for organic materials such as pine tree needles (Umlauf et al., 1994; Simonich and Hites, 1995). In this respect, the pine species, *Pinus uncinata*, constitutes the dominant tree species at the timberline (1700-2400m) of the Central Pyrenees (Figure 22). This species can therefore be useful as sentinel plant for atmospheric pollution in these remote alpine-subalpine zones. In the present thesis, the potential of *Pinus uncinata* to monitor long-range transported pollution to the high-mountain lake Estany Redon (Central Pyrenees) is investigated. The concentrations in the leaves can be compared with atmospheric PCB data. Based on concentrations of PCBs in the air and leaves one can interpret the state of equilibrium and see if external factors, like temperature, have influence on this equilibrium. Since temperature decreases with increasing altitude the species has been measured in an altitude gradient between 1750 m and 2250m.

5.2.1.1 Sample collection and analytical procedure *Pinus uncinata* leaves

Samples between 1750m and 2250m were collected in March and June 2002 with pre-cleaned tweezers, stored in glass tubes and transported to Barcelona at < 0ºC. There, they were stored at –20ºC until analysis. Whole pine needles (1-4 g fresh weight) of each sample were Soxhlet extracted for 24 h in 100 mL DCM inside a pre-cleaned glassfiber cartridge (Whatman Ltd) containing 5 g Na_2SO_4 (Merck, Darmstadt, Germany). Internal standards of PCB#30 and PCB#209 were added to all samples and blanks before extraction. Then, the extract was evaporated until 0.5 mL by vacuum rotary evaporation and clean up with a two-layer column (diameter 1 cm) filled with slurry packing in hexane with 8 g of silica gel (Panreac, Barcelona, Spain) (bottom) and with 8 g neutral aluminium oxide (top). The column was topped with 0.5 g of Na_2SO_4. Aluminium oxide, silica gel and sodium sulphate were activated overnight at 400ºC, 120ºC and 110ºC, respectively. Aluminium oxide and silica gel were deactivated with 5% Milli-Q H_2O. The column was then eluted with 20 mL of hexane and additionally with 20 mL hexane: DCM (19:1 v/v) for PCB elution. The recovered fractions were vacuum evaporated to 0.5 mL, transferred to vials and then further concentrated under a gentle N_2-gas stream and redissolved in 50μL of isooctane.

5.2.1.2 Dry weight and hexane-extractable lipid content

Dry weight (DW) and hexane-extractable lipids (HEL) were determined from sample aliquots (0.5-2 g). These aliquots were dried at 100ºC for 24 hours in a hot air oven for DW. For HEL the dried needles were extracted two times with 20 mL of hexane in a ultrasonic bath for 15 minutes. The combined extracts were then vacuum evaporated to 0.5 mL and transferred to a pre-weighted vial where they were concentrated further under a gentle stream of N_2 until constant weight. HEL were calculated gravimetrically.

5.2.2 SPMDs

Semi-permeable membrane devices (SPMDs) have been used as time integrated monitoring systems to sample organic contaminants in the atmosphere of remote and less remote areas (Petty et al., 1993; Prest et al., 1995; Ockenden et al., 1998; Booij and van Drooge., 2001). SPMDs consist of a low-density polyester bag of 30cm length, 2.5cm wide, and with a wall thickness of 70μm, which is filled with a natural lipid or the modified lipid triolein (1,2,3-tri[cis-9-octadecenoyl]glycerol). Exposed to the atmosphere they absorb organic contaminants from the gas phase. Since the PCBs and HCB in the high-mountain atmosphere are predominantly situated in the gas phase, SPMDs can be used to measure their levels in the atmosphere over a period of months.

The uptake is governed by

$$N_s = C_a K_{sa} V_s (1\text{-}\exp[-k_e t]) \quad (1)$$

where N_s is the absorbed amount of contaminant in the SPMD, C_a is the concentration in the atmosphere, K_{sa} is the SPMD-air partitioning coefficient, V_s is the volume of the SPMD, k_e is the uptake rate and t is the exposure time. k_e is defined as

$$k_e = k_o A / k_{sa} V_s \quad (2)$$

where A is the exposure surface and k_o is the overall mass transfer coefficient, which is defined as

$$k_o^{-1} = (k_m K_{ma})^{-1} + k_a^{-1} \quad (3)$$

where k_m, k_a are the mass transfer coefficients for the membrane and for the air boundary layer, and k_{ma} is the membrane-air partitioning coefficient. So, the concentrations in air can be calculated from

$$C_a = N_s / (K_{sa} V_s [1\text{-}\exp(-k_e t)]) \quad (4)$$

The denominator in equation 4 can be interpreted as the effective air volume extracted by the SPMD during the exposure. The extracted air volume may differ between compounds because K_{sa} and k_e are compound-dependent.

When $k_e t \rightarrow 0$ (short exposure times), the term between brackets is close to zero. Moreover, equation 4 is not commonly used to calculate C_a. The usual method is to check for which compounds equilibrium is attained. For these compounds, C_a is calculated from the concentration in the SPMD and the SPMD-air partitioning coefficient (K_{sa}). For the compounds that have not attained equilibrium, a constant air-sampling rate is assumed. The k_oA limit set for choosing either method is arbitrary, and it is not obvious what to do when compounds attain 30 or 70% of their equilibrium concentration. The advantage of equation 4 is that it covers both extremes, as well as the intermediate situation when partial equilibrium is attained. The limiting cases for short and long exposure times of this equation are as follow.

Equilibrium is attained when $k_e t \rightarrow \infty$ (long exposure times). Then, equation 4 reduces to

$$C_a = N_s / K_{sa} V_s \quad (5)$$

which states that the concentration in air can be calculated from the concentration in the SPMD ($N_s / V_s = C_s$) and the partitioning coefficient (K_{sa}).

The SPMD-air partitioning coefficient Ksa is temperature dependent and is calculated by

$$K_{sa} = K_{sw}\, RT/H \qquad (6)$$

where K_{sw} is the SPMD-water partitioning coefficient obtained from Booij et al., (2003).

For small exposure times, the compounds are in the linear uptake mode. Making the Taylor series expansion of $\exp(-k_e\, t)$ around $k_e\, t = 0$

$$C_a = N_s / K_{sa} V_s\, k_e\, t \qquad (7)$$
$$= N_s / R_s\, t$$

which is the sampling rate equation, with

$$R_s = K_{sa} V_s\, k_e \qquad (8)$$

Since there are only few data on sampling rates by SPMD, the uptake kinetics can be evaluated using the (first order) dissipation rate constant of performance reference compounds (PRCs), which can be calculated from

$$k_e = - \ln (N / N_0) / t \qquad (9)$$

where N is the PRC amount remaining after the deployment, and N_0 is the amount that was initially present in the SPMD at $t = 0$. Usually, however, only a single PRC can be used to calculate k_e. Compounds with small K_{sa} values have completely dissipated, and there is nothing left to quantify. For compounds with high K_{sa} values, the decrease in amounts is often too small to quantify. When the exchange kinetics between air and SPMDs are controlled by the air boundary layer, some basic arguing can be used to calculate k_e values for all compounds from the measured k_e for one PRC. For boundary layer controlled uptake the overall mass transfer coefficient for the boundary layer ($k_o \approx k_a$)

$$k_e = k_a A / K_{sa} V_s \qquad (10)$$

PRC-based exchange rate coefficients (k_{e1}) can be used to calculate the coefficients for other compounds (k_{e2}) using

$$k_{e2} = k_{e1} (K_{sa1} / K_{sa2}) (k_{a2} / k_{a1}) \qquad (11)$$

There is general agreement in the literature that mass transfer coefficients for fluid boundary layers are inversely proportional to the 2/3 power of the molecular diffusion coefficient. Hence,

$$k_{e2} = k_{e1} (K_{sa1} / K_{sa2}) (D_{a1} / D_{a2})^{2/3} \quad (12)$$

The leading term in equation 12 is the ratio in SPMD-air partitioning coefficients, which may largely differ between compounds. The ratio of diffusion coefficients usually is quite small. For example, the difference in D_a between HCB and PCB#180 is only a factor of about 1.2.

Concentrations in air for all compounds may be calculated from the dissipation of a single PRC, provided that the exchange kinetics is boundary layer controlled. This condition may be relaxed for compounds that are more volatile than the PRC, because the PRC usually has attained some degree of equilibrium, and the more volatile compounds will have attained a larger degree of equilibrium, which allows for the application of equation 5 anyway.

For very short studies, where the extracted volume is too small to detect compounds in the SPMDs, or in studies of the gas- particulate phase partitioning, the passive sampling method with SPMDs is not useful. Here the conventional HiVol-sampler can be used. A drawback of the HiVol-sampler is that it needs electrical supply to pump air through the adsorption material. At remote sites, like high-mountain areas, this can only be done with the use of a generator. On the contrary, SPMDs are easy to handle, relatively cheap and can be exposed on any site, where they passively sample the atmosphere.

Figure 23. SPMD-sampler situated at Tuc deth Port de Vielha (2600m).

5.2.2.1 Sample collection and analytical procedure of SPMD

From March 2002 until June 2003 SPMDs were exposed to the atmosphere on the border of the high mountain lake Estany Redon (Central Pyrenees), and analysed on HCB and individual PCB congeners. Further more, pump samplings were performed simultaneously in the valley and on the mountain top, at 1600m and 2600m respectively, in the vicinity of Estany Redon (Figure 23).

SPMDs were exposed in duplicate during 3 sampling periods of 85, 161 and 210 days, between March 2002 and June 2003. The SPMDs were filled with 270mg spiked triolein (Sigma, 95%). Triolein was spiked with 40, 7, 7 ng of PCB#4, PCB#29 and PCB#155, respectively. None of these PCB appeared in the atmospheric samples. To protect the SPMDs against direct sunlight and wind they were hanged inside a sampler, which consists of an untreated wood pole with a zinc bucket upside down that was closed off with a steel wire screen. Similar samplers were used successfully in other studies (Booij and van Drooge, 2001). In all sampling periods two non-exposed SPMDs filled with spiked triolein were analysed as blank. Their amounts were substracted from the exposed SPMDs.

The SPMDs were stored and transported in closed glass bottles at –20ºC. A few hours before exposure and after exposure they were stored at 0ºC. Handling of SPMDs was done with pre-cleaned tweezers. After exposure the exterior of the SPMDs were wiped off with a tissue in order to remove eventually attached particles. Then, after cutting off the (triolein free) mounting loops, the SPMDs were extracted twice for 24h with 100ml hexane:DCM (4:1 v/v). Internal standards, PCB#30 and PCB#209, were added at the beginning of the first extraction period. The analytical recovery was studied twice using SPMDs that contained PCB spiked triolein. For each series, 2 SPMDs were used as for control purposes.

All extracts were concentrated to 0.5 mL. Clean up of extract was done by using a 8 g silica (5% H_2O) + 8 g aluminium oxide (5% H_2O) + 1 g Na_2SO_4 column with 20 mL hexane and 20 mL hexane/DCM (19/1 v/v). The collected fraction was then evaporated until 0.5 mL using vacuum rotary evaporation and further concentrated until 50 μL in iso-octhane under a gentle nitrogen stream.

5.2.3 Quantification of *Pinus uncinata* leaves and SPMD

Before injection 25 μL of tetrachloronaphthalene were added to the extracts to correct for variation in instruments and end volume. The extracts were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD; Hewlett-Packard 5890 Serie II) for the analysis of HCB, PCB congeners #18, #28, #52, #101, #110, #153, #138, #180. The GC was equipped with a fused silica capillary column DB5 (50 m x 0.25 mm i.d. x 0.25 μm film thickness; J&W Scientific, Folsom, CA). Nitrogen and helium were used as make up gas (60 mL min^{-1}) and carrier gas (0.33 mL min^{-1}). The oven temperatures were programmed from 100ºC (1 min) to 150ºC at 15ºC min^{-1}, following a heating of 4ºC min^{-1} until 240ºC (holding time 12 min.), and then to

300ºC at 4ºC min^{-1} with a final holding time of 10 min. Samples were injected in split/splitless mode at 280ºC. The detector temperature was 310ºC.

The external standard method was used for the identification of the peaks in the chromatograms corresponding to the different retention times of the compounds on the column and to quantify the OC. The concentration range of the external standards covered the range of compound concentrations found in the samples. The limit of quantification (LOQ) was calculated from the average blank value plus 3 times the standard deviation. Blank values of detected compounds were about 30-200pg. LOQs were between 100-500pg for analysed OC.

5.3 Soil

Soils on the Island of Tenerife, Estany Redon and Ladove Pleso were collected in 2001. All soil sample analyses were done by Dr. Sandra Ribes-Cartagena. The sampling and analytical procedure was the same for all samples.

5.3.1 Sample collection on Tenerife

On the island of Tenerife soil samples were collected on the north-eastern slopes at 26 different altitudes, from 10m up to 3400m. Prior to sample collection the fresh litter was removed. Then, between 19m and 2500m the upper 5cm of surface soils were collected with a soil corer. Samples above 2500m, who were very stony and dry, were sampled with a small shovel and shifted through 500µm. The samples wrapped in aluminium foil, packed in heat sealable polyester bags and stored at 4ºC until analysis (Ribes et al., 2002).

5.3.2 Sample collection in high-mountains

In the Central Pyrenees (Estany Redon) and the High Tatras (Ladove Pleso) a 7 cm (diameter) x 20 cm (long) stainless steel cylinder was used for soil core collection. All soils were taken in the lake catchment areas. They were then immediately divided in sections of 2 and 0.5 cm, respectively, and stored in pre-cleaned aluminium foil at –20°C until analysis.

5.3.3 Analytical procedure of soil samples

Soils were weighted into a Whatman Soxhlet cellulose thimble. About 1:1 w/w sodium sulphate was mixed with the soil samples in order to improve Soxhlet extraction by water removal. Prior to extraction, samples were spiked with PCB congeners #30 and #209, which were used as surrogate standards. In Table 7 the recoveries of soil extraction method are presented. Samples were extracted with hexane:DCM (4:1 v/v) for 18 h. All extracts were first concentrated by rotary vacuum evaporation to 3-5mL and subsequently eluted through an anhydrous sodium sulphate column. After rotary vacuum evaporation to ~0.5mL, the extracts were fractionated on a neutral

aluminium oxide column (2g) and fractions were eluted with with 8mL of hexane:DCM (9:1 v/v) and 10mL of hexane:DCM (1:2). About 0.5g activated copper (size<63μm) (Merck, Darmstadt, Germany) were added to OC fraction. Copper powder was activated by sonification with 25% hydrochloric acid (3x 5mL) (Merck, Darmstadt, Germany) and then it was rinsed several times with Milli-Q water to neutral pH and, subsequently, with acetone for removal of water. After manual steering the suspensions were kept overnight at room temperature. This copper powder was removed by filtration though glass wool and rinsed with *n*-hexane. Elution solvent and rinses were concentrated to 50μL in isooctane after rotary vacuum and nitrogen stream evaporation.

5.3.4 Quantification of soil samples

The following OC were determined in the soil cores: PAH, HCB, α-HCH, β-HCH, γ-HCH, δ-HCH, DDTs and PCB congeners #18, 28, 52, 70, 101+90, 110, 149+123, 118, 153, 132+105, 138, 160+158, 180, 194 and 199. Identification and quantification of the organochlorine compounds were the same as the method used for the atmospheric samples (paragraph 5.1.5.1 and 5.1.5.2 for OC and PAH, respectively).

5.3.5 TOC in soils

Soil samples were extracted with HCl (3N) to remove the inorganic carbon. Subsequently, they were cleaned with Milli-Q water until neutral pH (7±2) and dried at 60ºC. The determination of total organic carbon (TOC) was performed by flash combustion at 1025ºC followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. These analyses were done by the Laboratory for Micro-analysis (IIQAB-CSIC, Barcelona, Spain).

5.3.6 Black-carbon (BC)

Black carbon was determined by the chemo-thermal oxidation (CTO) method (Gustafson and Dickhut, 1997; Gustafsson et al., 2001). In this thesis BC refers to the measurements with this CTO method, which in some cases may be similar to the soot-carbon. The BC analyses were done by Dr. Ørjan Gustafsson (ITM, Stockholm University, Sweden).

5.4 Sediments

The sediment cores of Estany Redon, Dlugi Staw and Starolesnianske Pleso have been sampled for the MOLAR project in 1996. The analyses were done by Dr. Pilar Fernandez and Dr. Rosa M. Villanova. The sediment core of Ladove Pleso was collected in September 2001 and analysed for the EMERGE project. In all cases the sampling and analytical procedures were the same (5.4.1). All samples were analysed on their TOC content and their age. The methodologies for TOC determination and core dating are presented in 5.4.3 and 5.4.4, respectively.

5.4.1 Sample collection and analytical procedure of high-mountain lake sediments

Samples were obtained by using a gravity coring system (Glew, 7.5cm diameter; 30cm long) for sediment coring in the deepest point of the lake. At shore, sediment cores were immediately divided in sections of 2 and 0.5cm, respectively (0.3 and 0.25cm in the case of Redon and Ladove sediments, respectively), and stored in pre-cleaned aluminum foil at –20°C until analysis in laboratory. Wet sediment sections were extracted by sonification with methanol (1x20mL; 20 min.) and, subsequently, with DCM-methanol (2:1 (v/v); 3x20mL; 20 min.). PCB#30 and PCB#209 standards, together with deuterated anthrancene and benzo(ghi)perylene, were added to combined extracts. The recoveries of the surrogates are presented in Table 7. Then, the extracts were vacuum rotary evaporated until 10mL. They were hydrolyzed overnight with 20mL of 6% KOH (Panreac, Spain) in methanol. The neutral fractions were recovered with *n*-hexane (3x10mL), and vacuum rotary evaporated until 0.5mL. The extracts were then transferred to a glass column (35cm x 0.9 i.d) packed with 2g of activated aluminium oxide. OC were collected in the first fraction with 5 mL of *n*-hexane-DCM (19:1 (v/v)). PAH were collected in the second fraction with *n*-hexane-DCM (1:2 (v/v)). About 0.5g activated copper was added to OC fraction. Then the fraction was transferred to another flask. Both, OC and PAH fractions were vacuum rotary concentrated until 1 mL and further concentrated until 50μL in iso-octhane under a gently nitrogen stream. Extracts were stored at –20ºC before injection in gas-chromatograph.

5.4.2 Quantification of sediment samples

In sediments, PAH, HCB, DDTs and the polychlorobiphenyl congeners #28, 52, 101+90, 149+123, 118, 153, 138 and 180 were determined. In addition, PCB congeners #70, 110, 132+105, 160+158, 194 and 199 were also analysed in the sediment core of Ladove Pleso. Identification and quantification of the organochlorine compounds was the same as the method used for the atmospheric samples (paragraph 5.1.5.1 and 5.1.5.2 for OC and PAH respectively).

5.4.3 TOC in sediments

Sediment samples were extracted with HCl (3N) to remove the inorganic carbon. Subsequently, they were cleaned with Milli-Q water until neutral pH (7±2) and dried at 60ºC. The determination of TOC was performed by flash combustion at 1025ºC followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. These analyses were done by the Laboratory for Micro-analysis (IIQAB-CSIC, Barcelona, Spain).

5.4.4 Core dating

In 4.3.2 it was already mentioned that the chronology of sediment accumulation is estimated from the changes in concentrations of natural radioactivity. Sediment samples were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay using Ortec HPGe GWL series

well-type coaxial low background intrinsic germanium detectors (Appleby et al., 1986). ^{210}Pb was determined via its gamma emissions at 46.5 keV and ^{226}Ra by the 295 keV and 352 keV γ-rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662 keV and 59.5 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy γ-rays within the sample (Appleby et al., 1992). Supported ^{210}Pb activity was assumed to be equal to the measured ^{226}Ra activity. Unsupported ^{210}Pb activity was calculated by subtracting supported ^{210}Pb from the measured total ^{210}Pb activity. ^{210}Pb radiometric dates were calculated using the CRS and CIC dating models (Appleby and Oldfield, 1978). These dates were validated against the 1986 and 1963 depths determined from the ^{137}Cs/^{241}Am stratigraphic records. The core datings were done by Dr. Peter Appleby (University of Liverpool, UK).

Table 7. Recoveries of surrogates in different sampling methods.

	PCB30	PCB209	Anthrancene-d10	Benzo(ghi)perylene-d10
Atmosphere (gas)	80 ± 8%	92 ± 17%	95 ± 19%	74 ± 21%
(part.)	73 ± 10%	83 ± 16%	89 ± 14%	68 ± 28%
Deposition	77 ± 18%	78 ± 11%		
Pinus uncinata	82 ± 10%	89 ± 20%		
SPMD	87 ± 21%	87 ± 17%		
Soil	70 ± 14%	95 ± 25%	Na	82 ± 25%
Sediment	69 ± 11%	82 ± 11%	65 ± 14%	79 ± 18%

na = not analysed

Chapter 6 Results

Chapter 6. Results

The results of the accomplished studies in this PhD-thesis are presented here in the form of articles. Some of them are published in scientific journals, while others are submitted for publication. They include:

1. van Drooge, B.L., Grimalt, J.O., Torres-García, C.J., Cuevas, E., 2002, **Semivolatile oragnochlorine compounds in the free troposphere of the northeastern Atlantic**, Environmental Science & Technology, 36, 1155-1161.

Barend L. van Drooge: Sampling, analyses and interpretation
Joan O. Grimalt: Supervisor of PhD-thesis of BLVD, interpretation
Carlos J. Torres-García: Sampling, meteorological calculations, interpretations
Emilio Cuevas: Support with meteorological data, interpretation

2. van Drooge, B.L., Grimalt, J.O., Torres-García, C.J., Cuevas, E., 2001, **Deposition of semi-volatile organochlorine compounds in the free troposphere of the eastern North Atlantic Ocean**, Marine Pollution Bulletin, 42, 628-634.

Barend L. van Drooge: Sampling, analyses and interpretation
Joan O. Grimalt: Supervisor of PhD-thesis of BLVD, interpretation
Carlos J. Torres-García: Sampling, meteorological calculations, interpretations
Emilio Cuevas: Support with meteorological data, interpretation

3. Ribes, S., van Drooge, B., Dachs, J., Gustafsson, Ø., Grimalt, J.O., 2003, **Influence of soot carbon on the soil-air partitioning of polycyclic aromatic hydrocarbons**, Environmental Science & Technology, 37, 2675-2680.

Sandra Ribes: Sampling and analyses of soil samples, interpretation
Barend van Drooge: Sampling and analyses of air samples, interpretation
Jordi Dachs: Modeling of PAH soil-air partitioning, interpretation
Ørjan Gustafsson: Analyses of SC, interpretation
Joan O. Grimalt: Supervisor of PhD-thesis of SR and BLVD

4. van Drooge, B.L., Grimalt, J.O., Camarero, Ll., Catalan, J., Stuchlík, E., Torres-García, C.J. Submitted. **Atmospheric semi-volatile organochlorine compounds in european high mountian areas (Central Pyrenees and High Tatras)**, Environmental Science & Technology.

Barend L. van Drooge: Sampling, analyses and interpretation
Joan O. Grimalt: Supervisor of PhD-thesis BLVD, interpretation
Jordi Catalan: Sampling in the Pyrenees, interpretation
Lluis Camarero: Sampling in the Pyrenees, meteorological data, interpretation
Evzen Stuchlík: Sampling in the High Tatras, meteorological data, interpretation
Carlos J. Torres-García: Calculation of air mass back-trajectories, interpretation

5. van Drooge, B.L., Grimalt, J.O. submitted. **PCBs in *Pinus uncinata*, the uppermost growing tree species of central pyrenean high mountains (Catalonia, Spain)**, Chemosphere

Barend L. van Drooge: Sampling, analyses and interpretation
Joan O. Grimalt: Supervisor of PhD-thesis BLVD, interpretation

6. van Drooge, B.L., Grimalt, J.O., Booij, K., Camarero, Ll., Catalan, J. Submitted**. Passive sampling of atmospheric organochlorine compounds by SPMDs in a high-mountain area (Central Pyrenees)** Environmental Science & Technology.

Barend L. van Drooge: Sampling, analyses and interpretation
Joan O. Grimalt: Supervisor of PhD-thesis BLVD, interpretation
Kees Booij: Development of SPMD technique, interpretation
Jordi Catalan: Sampling, interpretation
Lluis Camarero: Sampling, meteorological data, interpretation

7. Grimalt, J.O., van Drooge, B.L., Ribes, A., Vilanova, R.M., Fernàndez, P., Appleby, P., 2004, **Persistent organochlorine compounds in soils and sediments of European high altitude mountain lakes**, Chemosphere, 54, 1549-1561.

Joan O. Grimalt: Supervisor of PhD-thesis of BLVD, AR and RMV, interpretation
Barend L. van Drooge: Analyses of Ladove Pleso, interpretation
Sandra Ribes: Analyses of soil samples, interpretation
Rosa M. Vilanova: analyses of Starolesnianske Pleso, Dlugi Staw and Estany Redon, interpretation
Pilar Fernàndez: Supervisor of PhD-thesis RMV, interpretation
Peter Appleby: Radiometric dating, interpretation

8. Grimalt, J.O., van Drooge, B.L., Ribes, A., Fernàndez, P., Appleby, P. Submitted. **Polycyclic aromatic hydrocarbon composition in soils and sediments of high altitude lakes.** Environmental Pollution

Joan O. Grimalt: Supervisor of PhD-thesis of BLVD and AR, interpretation
Barend L. van Drooge: Analyses of Ladove Pleso, interpretation
Sandra Ribes: Analyses of soil samples, interpretation
Pilar Fernàndez: analyses of Starolesnianske Pleso, Dlugi Staw and Estany Redon, interpretation
Peter Appleby: Radiometric dating, interpretation

9. van Drooge, B.L., Grimalt, J.O., Axelman, J., Gustafsson, Ø., Jones, K.C., Stephanou, E. Submitted. **Congener specific assessment of global atmospheric PCB pool.** Environmental Science & Technology.

Barend L. van Drooge: Analyses of atmospheric samples from Tenerife, interpretation
Joan O. Grimalt: Supervisor of PhD-thesis BLVD, interpretation
Johan Axelman: interpretation
Ørjan Gustafsson: interpretation
Kevin C. Jones: interpretation
Euripides Stephanou: interpretation

The presented results are discussed in Chapter 7 of this thesis, which is divided in three blocks.

- Atmospheric transport and fate of POP in the subtropical troposphere (article 1 – 3)

- Atmospheric transport and fate of POP in European high-mountain areas (article 4 – 8)

- Global atmospheric fate of POP with PCBs as model compounds (article 9)

Article 1.

SEMIVOLATILE ORAGNOCHLORINE COMPOUNDS IN THE FREE TROPOSPHERE OF THE NORTHEASTERN ATLANTIC

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Research

Semivolatile Organochlorine Compounds in the Free Troposphere of the Northeastern Atlantic

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Polychlorobiphenyls (PCBs), hexachlorobenzene (HCB), hexachlorocyclohexanes, and DDTs were analyzed over 1 entire year period in the air of a high altitude remote site (2367 m above sea level) located in Teide (Tenerife, Canary Islands, 28°N16°W) in the Eastern North Atlantic region. Twenty samples were collected providing information on the concentrations of these semivolatile organochlorine compounds (SOCs) in the free troposphere since the stable and persistent temperature inversion in the subtropics defines a clear separation from the marine boundary layer. More than 80% of total SOCs were in the gas phase. HCB was the individual SOC in higher concentration, 51 pg m^{-3}, well above than the other SOCs identified, 1−11 pg m^{-3}. Sum PCB concentrations were 78 pg m^{-3}. These concentrations range among the lowest described in atmospheric samples. The collected air originated from four main sectors, high and middle latitudes in the north Atlantic, Europe, and Africa, as determined from isentropic backward air mass trajectories. No significant differences were observed for the concentrations of these compounds between air masses showing a high uniform SOC composition of the free troposphere. Only the more volatile PCB congeners, #18 and #28, exhibited significant differences between air masses from northern and southern latitudes. A seasonal temperature dependence for the less volatile PCB congeners, five or more chlorine subtituents, was also observed. Free tropospheric concentrations of all SOCs except HCB were lower than those measured near sea level for reference. PCB concentrations at the two altitudes exhibited consistent differences according to degree of chlorination. The stronger decrease of the more volatile compounds with altitude might reflect higher photodegradation.

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Introduction

Several studies have documented the occurrence of semivolatile organochlorine compounds (SOCs) in the atmosphere of remote areas, where these environmentally persistent pollutants were not used neither produced (*1*−*3*). These results have shown the importance of the atmosphere for the transport of SOCs to these remote sites and for their distribution through air−soil and air−water exchange (*4*−*6*). However, full understanding of the role of the atmosphere in the global distribution of these compounds also requires the investigation of their occurrence in the free troposphere, far away from interactions with the continental and oceanic boundary layers. To our knowledge, this problem has only been addressed once from aircraft measurements (*7*).

In the present study, air samples were collected in the subtropical Northeastern Atlantic area. The meteorological conditions in this region are under the influence of the descendent branch of the Hadley cell, which basically consists on an energy net flux transport from the equator to the pole, and produces an area of strong subsidence circulation in the middle and lower troposphere at around 30°N (*8*). This circulation results in a dry and dynamically stable free troposphere, inhibiting convective processes. At sea level the circulation is dominated by the Trade-winds (NE winds) which transport relatively humid and cool air from middle latitudes. A stable temperature inversion separates the air masses below and above the boundary layer. This inversion obstructs vertical motions (Figure 1) and generates a typical stratocumulus sea-cloud between 900 and 2000 m above sea level.

In these subtropical latitudes, high altitude sites allow the continued sampling of free tropospheric air. The remote site selected for sampling has been the Izaña Atmospheric Observatory (IZO), situated at 2367 m above sea level in Teide (Tenerife Island, 28°18′N, 16°29′W; Figure 2), which is representative of background free tropospheric conditions and is not affected from local pollution sources.

Air samples were collected on a 15-m high tower during night time when the mountain-valley breeze system is well established. Twenty samples of gas and particulate phases were collected between June 1999 and July 2000, encompassing all year seasons. For reference of the SOC composition of air masses within the marine boundary layer, four samples were taken on the top of a 47-m high lighthouse ('Punta del Hidalgo', PHO) located at sea level at the northeastern part of the island (28°34′N 16°20′W). This location is open to the Trade-winds. Nineteen PCB congeners were analyzed in all samples, including tri- (#18, #28), tetra- (#52, #70), penta- (#90, #101, #105, #110, #118, #123), hexa- (#132, #138, #149, #153, #158, #160), hepta- (#180), and octachlorinated (#199, #194) congeners. Hexachlorobenzene (HCB), hexachlorocyclohexanes, α-HCH and γ-HCH, and 4,4′-DDT and 4,4′-DDE were also analyzed.

Materials and Methods

Back Trajectories. The origin of the air masses arriving to Tenerife was calculated from back-trajectories using the HIRLAM model (High-Resolution Limited Area Model) of the Spanish National Institute of Meteorology (INM). This model is based on isentropic surfaces that provide a more realistic representation than those elaborated from isobaric surfaces (*9*, *10*). The calculations were performed at 00:00 UTC and 12:00 UTC for 5 days (5-D) back with 1 h step. The isentropic surfaces for each back-trajectory at IZO and PHO

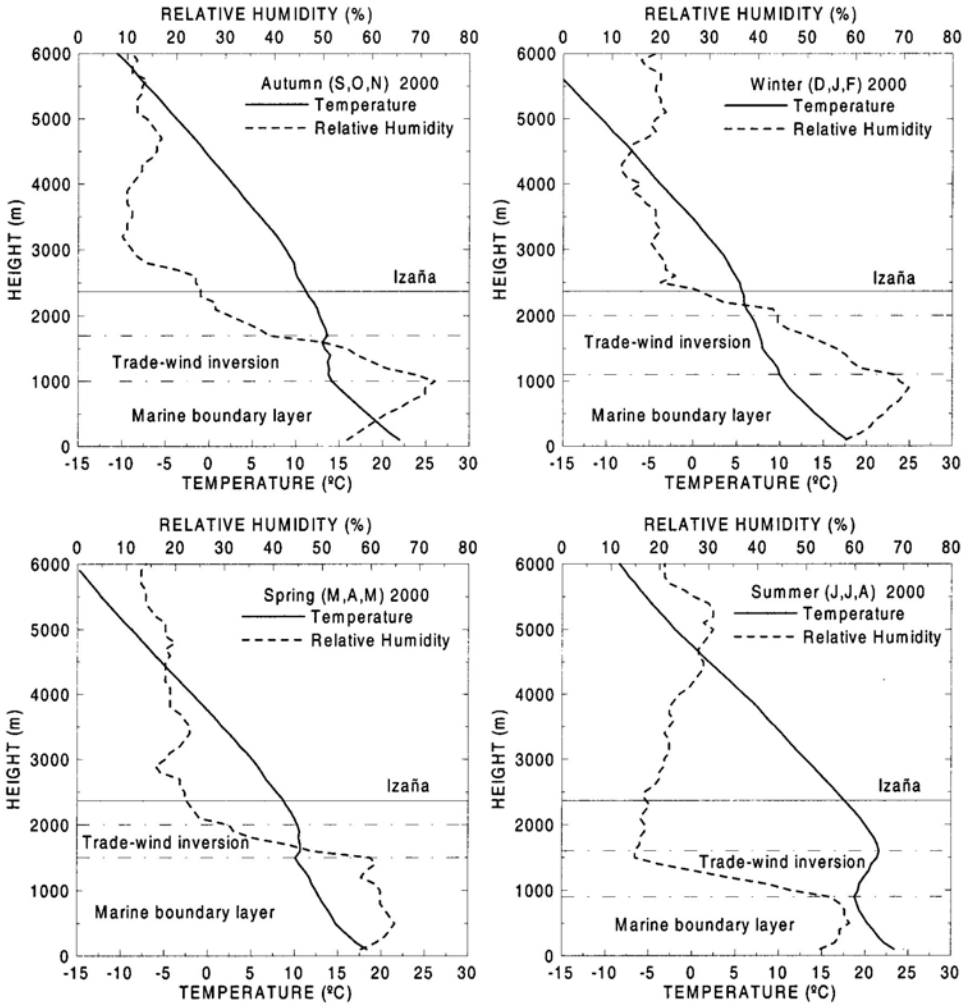

FIGURE 1. Averaged vertical profiles of temperature and relative humidity over Tenerife (28°18′N 16°29′W) for autumn, winter, spring, and summer. The profiles have been calculated with weekly ozone sonde data from Tenerife (#60020 Meteorological Station − INM) during year 2000. Trade-wind inversion is bounded by two dash−dot lines. The marine boundary layer is below the Trade-wind inversion.

stations were selected according to the observed potential temperature at 2367 and 47 m above sea level, respectively.

Sample Collection. Air was collected with a high volume sampler (MCV S.A., Collbato, Catalonia, Spain). SOCs in the gas phase were extracted from the air matrix with two polyurethane foam (PUF) plugs (diameter 6 cm; height 10 cm; density 28.5 kg/m^3) packed inside a Teflon tube. Glass fiber filters (GFF; Whatman International Ltd., Maidstone, England) were used to collect the particulate phase (20.3 × 25.4 cm; 1.0 μm pore size). Before sampling PUFs were Soxhlet extracted with *n*-hexane for 48 h. GFFs were cleaned by ashing at 400 °C for 24 h. PUFs were packed into the Teflon tubes which were subsequently wrapped in aluminum foil and introduced into heat sealed polyester bags (Kapak Corporation, Minneapolis, U.S.A.) for transport between Tenerife and Barcelona. GFFs were also wrapped in aluminum foil and introduced into polyester bags for transport. This was performed in approximately 2 days.

Collected sample volumes were between 80 m^3 and 240 m^3. After sampling, PCB#30 and PCB#209 were added as internal standards. The recoveries of these compounds were used to correct for losses during transport and analysis.

Sample Extraction and Analysis. PUFs and GFFs were Soxhlet extracted for 24 h in 250 mL of *n*-hexane (Merck, Darmstadt, Germany) and in 250 mL of hexane:dichloromethane (DCM; Merck, Darmstadt, Germany) (4:1 v/v), respectively. The extracts were vacuum evaporated until 1 mL. Samples and blanks were cleaned-up by adsorption on 2 g of aluminum oxide (Fluka Type 507C, Fluxa AG, Switzerland) and elution with 8 mL of hexane:DCM (9:1 v/v) and 7 mL of hexane:DCM (1:2 v/v). The collected fractions were vacuum evaporated to 1 mL and to near dryness under a gentle stream of nitrogen. Finally, they were redissolved in isooctane (Merck, Darmstadt, Germany) to 50 μL.

Tetrachloronaphthalene and octachloronaphthalene (Ehrenstorfer, Augsburg, Germany) were added to the vials before instrumental analysis for correction of possible instabilities. The extracts were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD, Hewlett-Packard 5890 Series II). A 50 m fused silica capillary column (0.25 mm

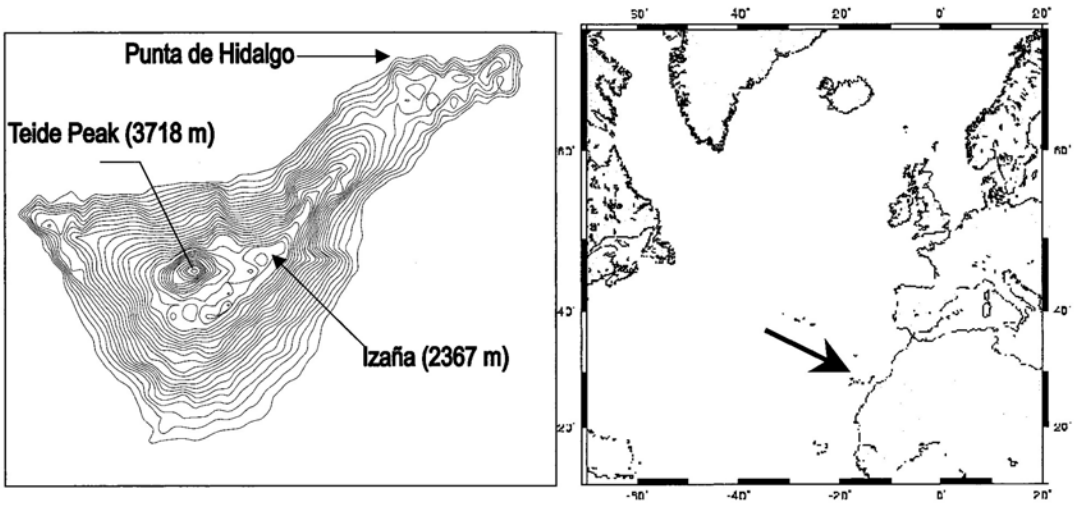

FIGURE 2. Location of the sampling sites in Tenerife Island.

i.d, 0.25 μm film thickness) coated with 5% phenyl 95% methylpolysiloxane (DB-5, J&W Scientific, Folsom, CA) was used for the analyses. The oven temperature program was started at 100 °C (holding time 1 min), increased to 150 °C at 15 °C/min, followed by heating at 4 °C/min to 240 °C (holding time 12 min), and finally increased to 300 °C at 4 °C/min (holding time 10 min). Injector and detector temperatures were 250 °C and 310 °C, respectively. Helium and nitrogen were used as carrier (0.33 mL/min) and makeup (60 mL/min) gases, respectively.

Quality Control and Assurance. Field blanks were inserted between the samples for monitoring for possible contaminations during transport and processing. These blanks were treated and analyzed as regular samples constituting about 30% of total samples analyzed. Field blank values were in the range of 1−10% of sample concentrations in the case of α-HCH, HCB, γ-HCH, PCB#28, PCB#90+101 and PCB#199, these levels were in the range of 10−20% for 4,4′-DDE, 4,4′-DDT, PCB#52, PCB#70, PCB#110, PCB#149+123, PCB#153, PCB#138, PCB#180, and PCB#194 and in the range of 20−30% for PCB#18, PCB#105+132, PCB#118, and PCB#160+158. For each batch of samples and blanks, sample concentrations were handled after subtraction of blank levels. Recoveries in PUF for PCB#30 and PCB#209 were 68 ± 20% and 77 ± 19%, respectively, and in GFF they were 66 ± 25% and 84 ± 17%, respectively. Injection of standards of the investigated SOCs into clean PUFs in Tenerife and subsequent transport and analysis in Barcelona gave recoveries between 81% and 118%. Detection limits (determined as three times the standard deviation of the chromatographic noise near the SOC peaks) were 0.04−0.23 pg m^{-3} for PCBs, 0.03 pg m^{-3} for HCB, 0.12 pg m^{-3} and 0.15 pg m^{-3} for α-HCH and γ-HCH, respectively, and 0.20 pg m^{-3} and 0.08 pg m^{-3} for 4,4′-DDE and 4,4′-DDT, respectively. PUF breakthrough was determined by injection of a mixture of PCB congeners #40, #155, and #185 into the first PUF plug before air adsorption of the regular sampling volumes. Replication of this test in four occasions did not show any traces of these compounds in the second PUF plug. Previous examination of possible adsorption effects into the filter by analysis of a second filter installed between the first filter and PUF showed that these could be in the level of 10% at the most which is consistent with other reports in the literature (*11*−*13*). The present results have therefore not been corrected by adsorptions in the second filter.

Results and Discussion

Free Troposphere Concentrations. More than 80% of all SOCs analyzed are in the gas phase (Table 1) which is in agreement with previous studies (*13*−*15*). HCB is the individual gas-phase SOC found in highest concentration at IZO (51 pg m^{-3}; Table 1). However, the summed PCB congeners are in higher abundance (78 pg m^{-3}; Table 1). The other SOC identified, α-HCH, γ-HCH, 4,4′-DDE, and 4,4′-DDT, are in much lower concentrations (1−11 pg m^{-3}; Table 1).

In the free troposphere, the average concentrations of α-HCH, γ-HCH, HCB, 4,4′-DDE, and 4,4′-DDT are lower than those reported at sea level in previous studies on remote sites such as the Arctic (*5*, *16*, *17*) and North Atlantic (*2*, *3*) oceans (Table 2). Transformation of the measurements reported in Table 1 to normal air volume (multiplication by a density factor of 1.4) still show that the samples collected at IZO exhibit lower values than in these previously studied remote sites. PCB are also in very low amounts in comparison to results previously reported in other remote sites. The normal volume average value of Σ PCBs at IZO is 109 pg m^{-3}. Only the sea level atmospheric concentrations reported at Spitsbergen (13 pg m^{-3} (*17*)) or ground level near Baikal Lake (89 pg m^{-3} (*16*)) are lower than this concentration (Table 2).

HCB, γ-HCH, and total PCB concentrations at IZO are also lower than those found in aircraft measurements between 2438 and 3048 m above sea level (*7*). However, the differences are within a factor of 2 at the most (Table 2). In contrast, this is not the case of α-HCH which in aircraft measurements was found to be about 50 times higher that at IZO (Table 2). These high aircraft α-HCH values range among the highest reported for remote sites (Table 2).

Temperature Dependence. Air temperatures at IZO range from 5.5 °C (average winter) to 17 °C (average summer). No temperature dependence has been observed for the changes in concentration of the pesticides and the PCB congeners with three or tetra chlorine substituents, but those with higher degree of chlorination exhibit temperature dependence. These dependences can be evidenced by representation of the natural logarithm of the concentrations vs the inverse of the absolute temperatures (*18*−*20*). The slopes and the correlation coefficients increase for the congeners with higher degree of chlorination, showing a strong negative correlation for PCB#180 (Figure 3). Higher temperatures involve higher

TABLE 1. Arithmetic Mean and Range of SOC Concentrations (pg m^{-3}) at the Two Sampling Sites, IZO (Izaña (2367 m asl)) and PHO (Punta de Hidalgo (47 m asl))

	PUF			GFF		
IZO (n = 20)	**mean**	**max**	**min**	**mean**	**max**	**min**
α-HCH	5.9	19	1.3	0.4	2.1	<0.12
HCB	51	110	23	0.4	3.7	<0.03
γ-HCH	11	37	1.6	1.0	9.1	<0.15
4,4′-DDE	4.2	6.9	1.1	0.4	1.6	<0.20
4,4′-DDT	1.0	3.0	<0.08	0.3	3.1	<0.08
PCB18	8.0	18	2.8	0.5	1.2	<0.07
PCB28	9.3	20	2.4	0.7	1.2	<0.2
PCB52	9.6	16	3.5	0.8	1.5	<0.19
PCB70	7.0	13	3.4	0.8	1.8	<0.05
PCB90+101	10	19	1.8	0.7	1.9	<0.12
PCB110	9.4	20	2.6	0.9	1.6	<0.08
PCB149+123	4.7	11	1.9	0.4	0.7	<0.1
PCB118	4.4	9.8	1.0	0.6	1.8	<0.02
PCB153	4.5	9.9	1.2	0.5	0.9	<0.12
PCB105+132	3.1	5.9	0.3	0.6	1.1	<0.15
PCB138	4.5	8.6	0.5	0.5	0.9	<0.15
PCB158+160	0.9	4.0	0.0	0.5	0.8	<0.15
PCB180	2.3	5.1	0.3	0.5	1.0	<0.15
PCB199	0.7	1.0	<0.15	<0.09		
PCB194	0.4	0.9	<0.15	<0.1		
ΣPCB	78	130	44	4.2	9.4	<1.7

	PUF			GFF		
PHO (n = 4)	**mean**	**max**	**min**	**mean**	**max**	**min**
α-HCH	22	25	19	0.6	0.9	0.4
HCB	72	79	69	<0.12		
γ-HCH	26	31	18	1.5	2.8	0.9
4,4′-DDE	22	29	11	2.2	2.5	2.1
4,4′-DDT	9.8	14	6.6	1.1	1.9	<0.08
PCB18	25	31	19	1.4	1.4	<0.07
PCB28	24	29	20	0.7	0.8	<0.2
PCB52	28	34	15	1.9	2.4	1.0
PCB70	23	28	16	1.4	1.8	1.0
PCB90+101	19	20	17	1.6	1.8	1.2
PCB110	18	19	16	3.1	3.5	2.6
PCB149+123	14	16	11	1.9	2.3	1.4
PCB118	7.7	11	5.1	1.7	2.0	1.6
PCB153	8.8	12	6.6	1.4	1.4	1.3
PCB105+132	8.0	9.6	6.3	1.4	1.7	1.2
PCB138	8.3	11	5.3	2.0	2.1	1.9
PCB158+160	3.7	6.9	1.9	0.5	0.6	0.4
PCB180	2.7	3.4	2.1	0.5	0.9	0.2
PCB199	0.3	0.4	0.3	<0.09		
PCB194	0.6	0.9	<0.15	<0.09		
ΣPCB	190	220	160	18	20	17

concentrations which is consistent from SOC degassing at warmer climate. This relationship is currently stronger near potential sources (*19, 20*). In this case, the restricted temperature dependence to the congeners with higher degree of chlorination is consistent with a PCB origin from diffuse sources reflecting long-range transport.

Back-Trajectories. Air masses sampled during the study had their origins over the northwestern Atlantic (North Atlantic High Latitude = NAHL), the western Atlantic (North Atlantic Mid Latitude = NAML), the western African continent (A), and western Europe (E; Figure 4). To evaluate whether geographical effects could be related to the occurrence of SOC, the samples have been grouped according to origin (Figure 4).

No significant differences (ANOVA, $p < 0.05$) are observed for the concentrations of the pesticides when comparing these four groups. HCB, HCH, and DDTs seem to be well mixed in the free troposphere (Figure 5). However, the relative content of 4,4′-DDT evidences some minor differences. Thus, air masses from the Atlantic (NAHL and NAML) exhibit very low 4,4′-DDT/(4,4′-DDT + 4,4′-DDE) fractions, 0.1 or <0.1, whereas in those originating from Europe and Africa this fraction is higher, 0.3−0.4, probably reflecting some influence of 4,4′-DDT residues from the continents (Figure 5).

The levels of α-HCH and γ-HCH are considerably lower than those found at other remote locations, namely in the case of α-HCH (Table 2). This difference is consistent with the banning of technical mixtures, α-HCH rich, in the past (*21*). Despite total isomers range between 13 and 23 pg m^{-3} between sectors significant differences are observed in the relative content of the α-isomer. The NAHL, NAML, Europe, and Africa air masses have α-HCH/(α-HCH+γ-HCH) fractions of 0.45, 0.39, 0.29, and 0.17, respectively. These differences are consistent with previous reports since α-HCH is found in higher relative amounts than γ-HCH in remote locations such as the eastern Arctic or the North Pacific Oceans (*1, 22*). Accordingly the higher relative content of α-HCH is found in NAHL and NAML, namely NAHL. In turn, the lower relative content of α-HCH of the samples originating from Europe and Africa, namely this last one, may reflect the recent use of γ-HCH in these continental areas.

The average concentrations of sum PCB in the four backward trajectory sectors are 67.5, 99, 75, 64 pg m^{-3} for NAHL, NAML, Europe, and Africa, respectively (Figure 5). Overall analysis of variance of these four sectors shows the absence of significant differences for the concentrations of nearly all PCB congeners. Only the lighter PCB congeners #18 and #28 show significant differences between these sectors ($p < 0.005$ and $p < 0.05$ in the ANOVA tests, respectively; Table 3). The differences involve a higher concentration in the air masses originating from southern middle latitudes. Thus, comparison of means between the southern middle (NAML + Africa) and the northern (NAHL + Europe) sectors, 11 and 6 pg m^{-3} for #18 and 13 and 7 pg m^{-3} for #28, respectively, shows significant differences ($p < 0.005$). This difference is essentially due to the influence of the air masses from Africa, which are those showing most distinct composition with respect to the other sampled air masses (Table 3). However, the concentrations of #18 and #28 in NAML air masses, 10−12 pg m^{-3}, also show a distinct composition from the air masses originating from NAHL, with concentrations of #18 and #28 5−6 pg m^{-3} ($p < 0.05$, Table 3). In contrast, there were no significant differences between the two northern sectors (NAHL and Europe), showing that the air masses from Europe do not necessarily reflect higher background PCB concentrations, as measured in former studies (*23*). However, it is possible that the European air masses arriving to IZO could have never been in direct contact with potential pollution sources, since they were travelling at high altitudes as calculated with the HIRLAM-model. Differences in composition between the African and the other air masses also involve compounds #105+132 (Africa-NAHL and Africa-Europe), #70 (Africa-NAML), and #153 (Africa-NAML), representing lower concentrations of these congeners in Africa (Table 3).

Evaluation of the PCB distributions of these air masses provides further insight into the differences in composition. NAHL, NAML, and Europe exhibit a close composition (Figure 5). This homogeneity contrasts with the results on PCB concentrations measured in other studies near sea level, or at lower altitudes, where a geographical effect could be recognized (*23, 24*). In the samples collected at IZO, the significant differences only concern the African sector (Table 3). The higher abundance of PCB#18 and PCB#28 in this sector involves a statistically significant lower relative content of congeners such as #110, #70, #153, and #105/#132 (Table 3). This higher abundance of PCB#18 and #28 could reflect a higher temperature enhancement of the more volatile PCB congeners over the African continent. In addition, sampled

TABLE 2. Comparison of the Atmospheric SOC Concentrations at Tenerife with Those from Other Remote Sites Reported in the Literature[a]

ref	sampling year	location	height (masl)	ΣPCB	α-HCH	γ-HCH	HCB	44′-DDE	44′-DDT
(*7*)	1986	Bermuda	3000	160[a]	300	16	98		
			500	330[a]	120	43	89		
(*17*)	1991	Lake Baikal		89[b]	490	105	190	8	8
(*18*)	1992	Spitsbergen		13[c]	140	32	205		
(*3*)	1992−1993	Bermuda	23	150[d]					
(*23*)	1996	E. Arctic Ocean			37	17			
(*2*)	1989−1990	N.Atlantic		290[a]	200	66		3	4
	1999−2000	Tenerife	2367	78	6	11	51	4	1
			47	190	22	26	72	22	10

[a] Different PCB congeners are considered in each case complicating comparison between different studies. The values indicated in this table correspond to the sum of the congeners considered in this study as indicated in the Introduction section: (a) no data on individual congeners reported by the authors; (b) #28, 52, 70, 101, 110, 118+149, 153+105+132, 138, 180; (c) #28, 31, 52, 101, 105, 118, 153, 156, 180; #18, 28, 52, 70, 101, 110, 149, 118, 153, 138, 180; (d) #18, 28, 52, 70, 101, 110, 149, 118, 153, 138, 180.

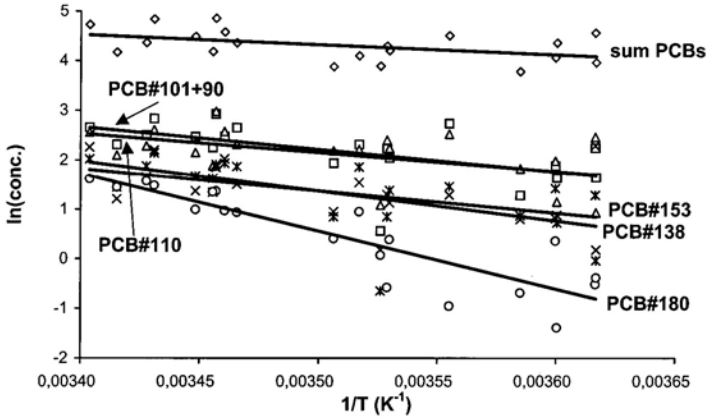

FIGURE 3. Dependences between air PCB congener concentrations and temperature. Sum PCB ($y = -1983/T + 11.3$; $r^2 = 0.20$), PCB101+90 ($y = -4540/T + 18.1$; $r^2 = 0.31$), PCB153 ($y = -4478/T + 17$; $r^2 = 0.27$), PCB110 ($y = -3833/T + 16$; $r^2 = 0.26$), PCB138 ($y = -6059/T + 23$; $r^2 = 0.36$), and PCB180 ($y = -11681/T + 41$; $r^2 = 0.77$). Concentrations in pg m^{-3}.

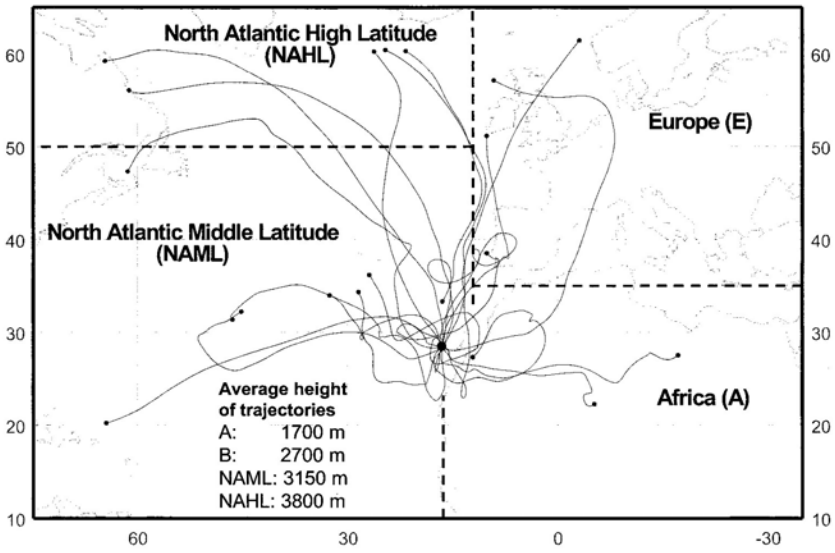

FIGURE 4. Isentropic back-trajectories of the samples collected at IZO between June 1999 and July 2000.

air masses from Africa originated near the ground in the Saharan desert which could facilitate the incorporation of these trichlorinated PCB congeners.

Vertical Distributions. Although the sampling strategy of this study was devoted to determine the concentrations in the free troposphere, as indicated above, some samples

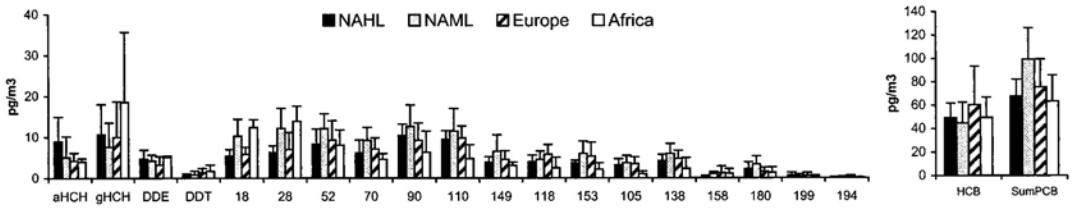

FIGURE 5. Mean SOC concentrations in the four sectors of IZO.

TABLE 3. Bilateral *t*-Test Comparison of the Means of the PCB Congener Concentration and Relative Distributions of the Air Masses Corresponding to the Samples Collected in the Free Troposphere at IZO[c]

	NAHL				NAML				Europe			
NAML	**congener**	**mn_{NAML}**	**mn_{NAHL}**	**sig.**								
					Concentrations							
	#18	10	5	$p < 0.05$								
	#28	12	6	$p < 0.05$								

Europe	**congener**	**mn_{Europe}**	**mn_{NAML}**	**sig.**
	#18	6	10	$p < 0.05$

Africa	**congener**	**mn_{Africa}**	**mn_{NAHL}**	**sig.**	**congener**	**mn_{Africa}**	**mn_{NAML}**	**sig.**	**congener**	**mn_{Africa}**	**mn_{Europe}**	**sig.**
	#18	12	5	$p < 0.01$	#70	4.5	9.1	$p < 0.05$	#18	12	6	$p < 0.01$
	#105/132	1.0	3.2	$p < 0.05$	#153	2.1	6	$p < 0.05$	#105/132	1	3.5	$p < 0.05$
					#105/132	1.0	3.7	$p < 0.05$				

	NAHL				NAML				Europe			
Africa	**congener**	**mn_{Africa}**	**mn_{Europe}**	**sig.**	**congener**	**mn_{Africa}**	**mn_{NAML}**	**sig.**	**congener**	**mn_{Africa}**	**mn_{Europe}**	**sig.**
					Relative Distributions[b]							
	#18	0.87	0.50	$p < 0.05$	#28	0.97	0.77	$p < 0.05$	#110	0.33	0.86	$p < 0.05$
	#28	0.97	0.57	$p < 0.005$	#70	0.33	0.65	$p < 0.05$	#153	0.17	0.44	$p < 0.05$
	#110	0.33	0.85	$p < 0.05$	#105/132	0.07	0.23	$p < 0.05$	#105/132	0.07	0.32	$p < 0.01$
	#105/132	0.07	0.30	$p < 0.001$								

[a] The origins of these air masses were calculated from backward air mass trajectories: Europe, Africa, and North Atlantic high and medium latitudes, NAHL and NAML, respectively. Mean PCB relative distributions are summarized in Figure 5. Nonreported cases, e.g. most PCB congeners, did not show significant differences between any of the air masses of different origins, pointing to a rather uniform PCB composition. [b] Percent with respect to maximum PCB congener concentration.

have been measured close to sea level at Tenerife for reference. PCB concentrations at PHO, 191 pg m^{-3}, are similar to those reported at sea level near Bermuda (150 pg m^{-3} (*3*)), higher than those found near Lake Baikal (89 pg m^{-3} (*16*)) or at Spitzbergen (13 pg m^{-3} (*17*)) and lower than those reported in the North Atlantic (290 pg m^{-3} (*2*)). HCB at PHO, 72 pg m^{-3}, is lower than in other sea level remote sites, 120–200 pg m^{-3} (Table 2). HCH, 22 and 26 pg m^{-3} for the α- and γ- isomers, are also found in lower concentrations than in other remote sites, but the differences are more significant for the α- than for the γ-isomer (Table 2).

The air concentrations at IZO are significantly lower than those measured at PHO (Table 1). The ratios between average measurements are 2.5 for sum PCB and 1.4 for HCB, 3.2 and 2.5 for α- and γ-HCH, respectively, and 5.5 and 9.8 for 4,4′-DDE and 4,4′-DDT, respectively. *t*-Tests of significance between means show that the differences are significant in all cases ($p < 0.05$ or lower) except for some highly chlorine substituted PCB congeners, e.g. #158/160 and #180. Transformation of the measurements at IZO to normal air volumes using the above-mentioned factor of 1.4 reflects a vertical concentration difference for all compounds except HCB. The concentrations of this compound show a uniform distribution below and above the boundary layer.

The fraction 4,4′-DDT/(4,4′-DDT + 4,4′-DDE) at PHO is 0.3 being higher than the fraction at IZO for NAHL and NAML air masses, 0.1 or <0.1, but similar to the European and African air masses. This higher fraction suggests some contribution of 4,4′-DDT from the ground in the air masses within the boundary layer. On the other hand, the mean fraction of α-HCH/(α-HCH+γ-HCH) at PHO is 0.40, an intermediate value between the fractions observed at IZO for NAHL and NAML and higher than that in air masses from Europe and Africa.

PCBs at PHO within the boundary layer are dominated by the lighter congeners (tri- and tetrachloro substituted), whereas above the inversion, at IZO, the mixtures are dominated by pentachlorinated congeners. Comparison of the average normal volume concentrations between the two altitudes shows a progressive depletion from the more to the less chlorinated compounds with factors of 0.36, 0.43, 0.5, 0.56, and 0.77 for the tri-, tetra, penta, hexa-, and heptachlorinated congeners, respectively. These differences in PCB distributions cannot be explained by diffusion processes. Would this be the case, tri- and tetrachlorinated congeners would also dominate the PCB composition at IZO. The differences in composition might be an effect of photodegradation by hydroxyl radicals since, as shown under laboratory conditions (*25*), these compounds with lower degree of chlorination exhibit higher reaction rates with these oxidants.

In this respect, concentrations of hydroxyl radicals in summer at 30°N latitude are higher at 2000 m than at sea

surface (*26*). However, these differences, 25×10^5 and 15×10^5 molecules cm^{-3}, respectively, are smaller in the other seasons. Latitudinal concentration gradients are also observed for these reagents which involve higher levels at the warmer regions (*26*). These latitudinal differences may also be relevant during SOC atmospheric transport.

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Article 2.

DEPOSITION OF SEMI-VOLATILE ORGANOCHLORINE COMPOUNDS IN THE FREE TROPOSPHERE OF THE EASTERN NORTH ATLANTIC OCEAN

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Deposition of Semi-Volatile Organochlorine Compounds in the Free Troposphere of the Eastern North Atlantic Ocean

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Deposition samples were taken at a height of 2367 m above sea level (m.a.s.l.) on the Island of Tenerife from May 1999 until July 2000 and analysed for 19 polychlorinated biphenyl (PCB) congeners, hexachlorobenzene (HCB), hexachlorocyclohexanes (HCH) and DDTs. This site is located above the inversion layer, so samples represent background concentrations of the free troposphere. The average deposition fluxes of HCB, total HCH, DDTs and PCBs were 86, 400, 110 and 780 ng m^{-2} yr^{-1}, respectively, being lower than those reported at sea level in continental or marine areas. All compounds are generally found in higher abundance in the wet precipitation samples. However, these samples only represent a fraction, e.g. 33%, of the total deposition load. Annual mass balance calculations show that wet precipitation is essentially responsible for the deposition of the low molecular weight OC whereas dry deposition accounts for more than 50% of the higher molecular weight PCBs. © **2001 Elsevier Science Ltd. All rights reserved.**

Introduction

Several studies show that semi-volatile xenobiotic organochlorine compounds (OCs) are global pollutants found in sites where they were never produced nor used (Atlas and Giam, 1981; Ballschmitter, 1992; Iwata *et al.*, 1993). For instance, irrespective of the regulations that have drastically decreased the production of polychlorobiphenyls (PCBs), the atmospheric concentrations of these compounds in remote locations have not decreased or have decreased very little since 1970s (Panchin and Hites, 1994; Baker and Eisenreich, 1990). They are also resistant to biological, chemical and physical breakdown and tend to accumulate in organic materials (Erickson, 1997). This persistence is a cause of concern since some PCB congeners are likely to cause toxic effects at present concentration levels (Hooper *et al.*, 1990; Muir *et al.*, 1988; Porta *et al.*, 1999). Likewise, hexachlorobenzene (HCB) and DDTs are toxic and tend to bioaccumulate (Grimalt *et al.*, 1994; Porta *et al.*, 1999). Some hexachlorocyclohexanes (HCHs) have also this capacity for bioaccumulation and are potentially toxic.

The atmosphere seems to be the most important way for the distribution of OCs on a global scale, including transport to the marine system (Duce *et al.*, 1991; Ballschmitter, 1992; Iwata *et al.*, 1993; Tolosa *et al.*, 1997). Its large volume and the high speed at which air masses can move afford a high capacity for transport over long distances. However, one major question to be elucidated is the role of high altitude air masses, free from the influence of ground OC inputs, in the transport of these compounds and its significance for the marine environment. To this end, the study of OC atmospheric deposition fluxes in the free ocean troposphere provides a major clue for the understanding of the significance of long-range air transport to seawaters.

For this purpose, the present paper reports the deposition fluxes of these compounds at 2367 m.a.s.l. in Izaña (Tenerife, Canary Islands). This site is representative of the subtropical region of the northeastern North Atlantic Ocean. In this region (30°N), the descendent branch of the Hadley cell produces strong subsident circulation in the middle and low troposphere (Fig. 1). This circulation causes a dry and dynamically stable troposphere, inhibiting convective phenomena. At sea level the circulation is dominated by the trade-wind systems (NE-winds) which transport relatively humid and cool air from middle latitudes. A temperature inversion, characterized by a typical stratocumulus cloud layer between 1400 and 1800 m.a.s.l., separates both air masses obstructing vertical exchange (Wells, 1997).

The sampling site considered in this study was situated above the inversion layer with a predominant wind direction from the NW (direct ocean inputs). The

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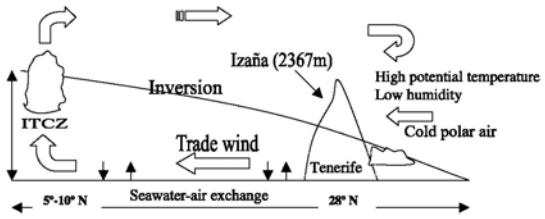

Fig. 1 General air circulation in the subtropical marine troposphere.

studied samples are representative of the free troposphere, not being affected from local and regional pollution sources.

Materials and Methods

Samples were taken at Izaña Meteorological Observatory (28° 18′N; 16° 29′W), on top of a tower of 15 m height. Atmospheric deposition was collected in stainless steel reservoirs ($\emptyset = 24$ cm, $A = 452.4$ cm^2) using a Model ARS 1010 sampler (MTX, Italy). Each sampling period encompassed approximately two weeks. After this time the reservoirs were carefully rinsed with Milli Q water in three successive steps and the rinses were collected together. Blanks were taken before each sampling. Both samples and blanks were filtered with pre-weighted glass microfibre filters (GFF) (Whatman, Maidstone, England (4.7 cm)). These filters were previously cleaned by ashing at 400°C for 24 h. After filtration the dissolved phase was extracted using Empore extraction C-18 disks (3M Empore, Harbor City, USA). Vacuum was used to increase the speed of filtration/extraction. PCB congeners #30 and #209 were introduced in both GFF and C-18 disks as internal standards before sample introduction. Then, the GFFs and C-18 disks were wrapped in aluminium foil, placed in polyester bags and stored at −20°C. These bags were introduced in portable refrigerators for air transport to Barcelona (approximately 2 days) where they were kept at 4°C.

The C-18 disks were successively extracted with methanol, cyclohexane and dichloromethane (5 ml each). Sample handling is described in detail elsewhere (Carrera *et al.*, 1998). Briefly, GFFs were Soxhlet extracted for 24 h in 100 ml of hexane:dichloromethane (DCM) (Merck, Darmstadt, Germany) (4:1 v/v), respectively. This extract was vacuum evaporated to 1 ml.

All samples and blanks were cleaned up with 2 g of alumina (aluminium oxide Fluka Type 507C, Fluxa AG, Switzerland) and 8 ml of hexane:DCM (9:1 v/v) (Merck, Darmstadt, Germany). The collected volume was vacuum evaporated to 1 ml and further concentrated to 50 µl in isooctane (Merck, Darmstadt, Germany) under a gentle stream of nitrogen. Tetrachloronaphthalene and octachloronaphthalene were added as internal standards before instrumental analysis for correction of possible instabilities.

The extracts were analysed by gas chromatography with electron capture detection (GC–ECD; Hewlett–Packard 5890) using a 50 m DB-5 column (J&W; id. 0.25 mm; film thickness 0.25 µm). The oven program started at 100°C for one min, increased to 150°C at 15°C/min and then to 240°C at 4°C/min holding this temperature for 12 min. Then, it was increased to 300°C at a rate of 4°C/min with a final holding time of 10 min. The detector and injector temperatures were 310°C and 250°C, respectively.

The 19 PCB congeners considered for study are representative of the total congeners present in higher abundance in environmental samples. These compounds and their respective mean blank values (pg) are as follows: #18 (0.16), #28 (0.05), #52 (0.14), #70 (0.15); #90 + #101 (0.23), #105 + #132 (0.13), #110 (0.17), #118 (0.07), #123 + #149 (0.07), #138 (0.13), #153 (0.08), #158 + #160 (0.012), #180 (0.03), #199 (0.001), #194 (0.0025). The HCH isomers considered for study, α-, β- and γ-, are also those currently found in higher abundance in environmental samples, their respective mean blank values were 0.09, 0.01 and 0.18 pg, respectively. No β-HCH was measured above detection limit (0.01 pg) in any of the samples. Blank values for *pp′*-DDE and *pp′*-DDT were 0.1 and 0.005 pg, respectively. The reported values have been subtracted for blank values in all cases.

Results and Discussion

Thirteen atmospheric deposition samples were collected during the sampling period, from 20 May 1999 until 4 July 2000, each encompassing about 15–25 days (Table 1). These deposition samples involve 234 days of collection. Over one year period (20 May 1999–19 May 2000) they represent 213 days, 58% of total. Dry and wet precipitation was collected in four samples (69 days, 33% of total sampling time) and only dry deposition in the rest. The collection time covered by these two types of samples is representative of the annual wet and dry periods at the sampling site.

Higher fluxes of organochlorine pesticides and PCBs are collected in the periods of wet and dry deposition than in the period of dry deposition only (Tables 1 and 2). The differences are very significant for HCHs, with increases of more than one order of magnitude for both α- and γ-isomers in the wet + dry period. The increase in *pp′*-DDE flux in wet + dry deposition is also near one order of magnitude higher than in dry deposition conditions. HCB and *pp′*-DDT increased 5 and 3.2 times in the wet + dry deposition samples, respectively. Although both series of data are not coincident in time, these strong differences are likely related to the different ways of deposition of the pesticides from the atmospheric pool. In fact, the atmospheric concentrations measured during the time of study at Izaña do not reflect major differences between the two periods.

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TABLE 1
Deposition fluxes of organochlorine pesticides in the free troposphere of the eastern Atlantic Ocean.[a]

Sampling start	Sampling days	α-HCH	HCB	γ-HCH	*pp*′-DDE	*pp*′-DDT
Dry deposition						
20 May 1999	15 (6)[b]	1.1	12	7.7	24	88
7 June 1999	15 (7)	1.9	11	8.5	23	32
24 June 1999	15 (–)	1.5	120	41	0.9	37
13 July 1999	14 (3)	6.1	18	6.6	11.5	30
30 July 1999	18 (7)	0.5	11	2.4	0	4.8
3 December 1999	17 (14)	54	35	130	47	9
10 January 2000	21 (7)	31	63	48	8.6	7
15 March 2000	21 (11)	13	3.5	61	37	27
14 June 2000	21 (–)	4	86	81	24	11
Mean		13	40	43	20	27
SD		18	41	43	16	26
Dry and wet deposition						
14 September 1999	15 (18)	210	89	630	140	47
9 October 1999	25 (13)	130	180	570	280	110
11 November 1999	14 (13)	680	390	1700	72	93
15 February 2000	15 (170)	110	190	880	130	100
Mean		280	210	950	160	87
SD		270	130	520	88	28
Total						
Mean		95	92	320	61	46
SD		190	110	510	80	38
%(dry + wet)/(dry + wet + dry only)		96	84	96	88	76

[a] The values are reported in ng m^{-2} yr^{-1} after normalization of the flux collected during the sampling period (ng m^{-2}) to annual values.
[b] Total deposition (mg) collected during the sampling period (– not available).

Since all these organochlorine compounds are essentially found in the gas phase (unpublished results), their increased deposition in the presence of water precipitation is probably influenced by their Henry constants (Ballschmitter and Wittlinger, 1991). Thus, the partitioning between gas phase and water dissolution is related to these constants (Wania, 1998). Accordingly, α-HCH and γ-HCH, the compounds with lowest Henry constants, 1.1 and 1 Pa m^3 mol^{-1}, exhibit highest deposition as wet + dry materials.

The fluxes observed for HCHs are significantly lower than those reported in south Norway, 2000–4000 ng m^{-2} yr^{-1} and 10 000–35 000 ng m^{-2} yr^{-1} for α-HCH and γ-HCH, respectively (Wania and Haugen, 1999) or Saskatchewan, 119 000 ng m^{-2} yr^{-1} for γ-HCH (Waite *et al*., 1999). They are also lower than the estimated (by calculation) average deposition over the North Atlantic, 4200 ng m^{-2} yr^{-1} for the summed HCH (Duce *et al*., 1991). The proportion between α and γ-isomers (1:3) is similar to that found in rural central Europe (1:3; Wittlinger and Ballschmitter, 1987). α-HCH dominates over γ-HCH in more remote locations such as the eastern Arctic or the North Pacific Oceans, (2:1 and 17:1, respectively; Harner *et al*., 1999; Atlas and Giam, 1981). The difference between very remote locations and sites receiving air masses from industrialized areas is attributed to the former use of HCH as insecticides in the form of technical mixtures containing high proportions of the α-isomer whereas, at present, only pure lindane (γ-HCH) is used (Harner *et al*., 1999). The HCH mixtures used in the past still dominate the composition in remote areas, e.g. due to revolatilization effects, whereas the γ-isomer dominates the HCH composition in industrialized areas (Harner *et al*., 1999).

HCB also exhibits lower values than those measured in the Mediterranean Sea, 240 ng m^{-2} yr^{-1} (Villeneuve and Cattini, 1986) or estimated over the North Atlantic, 310 ng m^{-2} yr^{-1} (Duce *et al*., 1991). The summed DDT fluxes are also lower than those calculated as likely average deposition over the North Atlantic, 280 ng m^{-2} yr^{-1} (Duce *et al*., 1991).

The average PCB fluxes are also lower than those reported elsewhere. Deposition values of 1400–7300 ng m^{-2} yr^{-1} are reported inland or near polluted sites such as Chesapeake Bay, Lakes Superior, Michigan, or near Wisconsin or Saskatchewan (Leister and Baker, 1994; Swackhamer and Armstrong, 1986; Franz *et al*., 1991; Swackhamer *et al*., 1988). The deposition values of Izaña are also lower or range in the lower end of those reported in marine areas such as the Swedish west coast (500–2300 ng m^{-2} yr^{-1}; Brorström-Lundén, 1998), Enewetak Atoll (North Pacific; 200–3000 ng m^{-2} yr^{-1}; Atlas and Giam, 1981) or those calculated as average deposition over the North Atlantic (1800 ng m^{-2} yr^{-1}, Duce *et al*., 1991).

The samples corresponding to combined dry and wet deposition involve higher atmospheric inputs of nearly all organochlorine compounds analysed (Fig. 2). However, over the whole year period, these samples only constitute about 33% of the total collection days. This rate is close to the annual percentage of wet precipitation days at Izaña Observatory. A deposition mass balance over a whole year period can therefore be estimated. The samples collected between 20 May 1999 and

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TABLE 2

Atmospheric input fluxes (ng m^{-2} yr^{-1}) of polychlorobiphenyls in the free troposphere of the eastern Atlantic Ocean.[a]

Sampling start[b]	#18[c]	#28	#52	#70	#90 + 101	#110	#149 + 123	#118	#153	#105 + 132	#138	#160 + 158	#180	#199	#194	Total
Dry deposition																
20 May 1999	0	0	0	225	35	58	160	29	232	80	204	39	190	0	19	1300
7 June 1999	28	41	54	30	360	190	78	44	5	110	71	11	14	0	7	1000
24 June 1999	190	46	0	0	79	43	52	0	56	88	33	23	4	7	4	630
13 July 1999	69	57	180	41	150	77	53	37	6	61	46	19	5	0	5	810
30 July 1999	1	13	25	0	6	0	7	0	4	11	0	4	2	0	0	73
3 December 1999	75	91	150	38	0	9	7	8	6	13	36	0	0	0	0	440
10 January 2000	53	0	20	0	0	0	16	0	6	0	23	0	0	0	0	120
15 March 2000	0	0	0	18	130	200	19	3	48	41	57	0	14	0	0	530
14 June 2000	0	0	0	44	170	260	16	3	13	20	25	0	0	0	0	550
Mean	51	31	63	45	100	90	42	15	38	52	53	11	25	2	3	620
SD	61	32	82	66	110	92	48	17	71	40	56	13	58	4	6	370
Dry and wet deposition																
14 September 1999	230	110	250	96	93	84	18	42	92	340	34	18	19	10	0	1400
9 October 1999	170	87	180	55	180	130	120	46	86	46	41	46	32	7	0	1200
11 November 1999	160	100	345	74	140	53	46	88	39	47	27	4	75	34	33	1300
15 February 2000	210	88	120	73	170	240	110	130	55	120	84	10	87	0	0	1500
Mean	180	92	210	67	170	140	93	87	60	70	51	20	65	14	8.2	1300
SD	28	9	120	11	20	95	41	41	24	41	30	23	29	18	20	140
Total																
Mean	80	45	98	50	120	100	53	32	43	56	52	13	34	5	6	790
SD	77	39	110	58	100	92	50	39	63	39	50	15	55	10	12	450
% (dry + wet)/ (dry + wet + dry only)	78	75	77	60	63	61	69	85	61	57	49	65	72	71	92	68

[a] These fluxes are normalized to annual values like the values reported in Table 1.
[b] Sampling periods as in Table 1.
[c] IUPAC congener numbers.

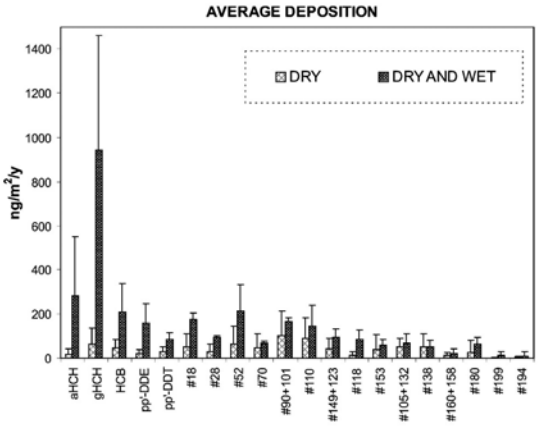

Fig. 2 Composition of the organochlorine pesticides and polychlorobiphenyl congeners in dry only and wet + dry depostion collected at Izaña Observatory. Interval bars indicate standard deviation. Numbers in abscissas refer to IUPAC PCB congener numbers. The flux values have been calculated by referencing the compound amounts deposited during the sampling time intervals to a whole year.

5 April 2000 (Tables 1 and 2), nearly an annual time interval, have been selected for calculation. The total load of organochlorine compounds represented by these samples shows that dry deposition is important for the incorporation of the higher molecular weight congeners (Fig. 3). In contrast, the proportion of organochlorine pesticides, particularly HCHs, and even low molecular weight PCBs, e.g. #18, #28, #52, is small in this mode of atmospheric precipitation.

Taking into account the annual wet precipitation rate, the results outlined in Fig. 3 show a scenario dominated by low deposition fluxes of organochlorine pesticides

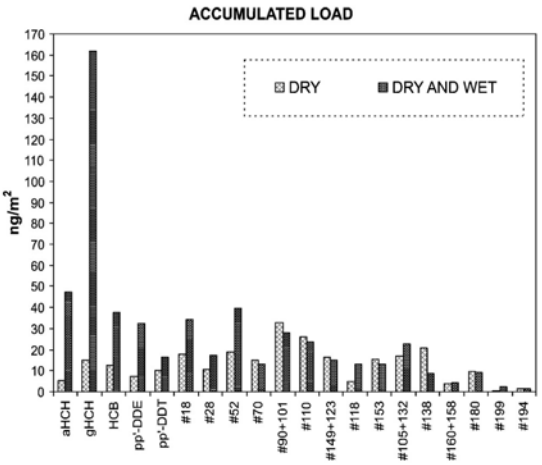

Fig. 3 Accumulated load of organochlorine compounds in the samples collected between 20 May 1999 and 19 May 2000 at Izaña Observatory. The days included in the collection periods represent 58% of the whole year. See Table 3 for scaling to one year cycle. Numbers in abscissas refer to IUPAC PCB congener numbers.

TABLE 3

Annual deposition fluxes (ng m^{-2} yr^{-1}) of organochlorine pesticides and polychlorobiphenyls calculated from mass balance integration of the input fluxes recorded in the samples collected over one year period (20 May 1999–5 April 2000) in the free troposphere of the eastern Atlantic Ocean.

Deposition type	α-HCH	γ-HCH	HCB	*pp'*-DDE	*pp'*-DDT	#18 [a]	#28	#52	#70	#90 + 101	#110	#149 + 123	#118	#153	#105 + 132	#138	#160 + 158	#180	#1 99	#194	Total
Dry	9.5	26	21	12	17	31	18	32	26	57	45	28	8.5	27	29	35	6.6	16	0.46	2.4	360
% of total	10	9.3	24	18	37	34	37	32	54	54	52	52	27	55	43	70	47	50	11	46	46
Dry and wet	82	280	65	56	29	59	30	68	22	48	41	25	23	22	39	15	7.3	16	3.8	2.8	420
% of total	90	90	76	82	63	66	63	68	46	46	48	46	74	45	57	30	52	50	90	54	54
Total	91	310	86	68	46	90	48	100	48	105	86	54	31	49	68	50	14	32	4.2	5.2	780

[a] IUPAC congener numbers.

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and PCBs. In association with the fall of dry particles, all compounds are incorporated at about similar fluxes, between 5 and 32 ng m^2, in this deposition mode (10 and 65 ng m^{-2} yr^{-1}, if these results are scaled to annual deposition, Table 3). In addition to this baseline flux, wet + dry deposition episodes involve high inputs of the lower molecular weight compounds, in the order of 20–48 ng m^{-2} (35–80 ng m^{-2} yr^{-1}, Table 3) for most compounds, and 162 ng m^{-2} for γ–HCH (280 ng m^{-2} yr^{-1}, Table 3), overcoming the dry deposition inputs.

This mass balance involves that 90% of HCH are incorporated as consequence of the sparse wet precipitation events. 76% and 82% of HCB and *pp′*-DDE are incorporated to the earth/sea surface by mediation of these wet episodes. Another group of compounds, *pp′*-DDT and PCBs #18, #28 and #52, exhibit an association to wet episodes of about 60% of the total load. Finally, these wet episodes are responsible of about 40–50% of the atmospheric higher molecular weight PCB, e.g. #70 or higher.

Conclusion

The average deposition fluxes of HCB, total HCH, DDTs and PCBs in the free troposphere (2367 m.a.s.l.) of the eastern North Atlantic Ocean are 86, 400, 110 and 780 ng m^{-2} yr^{-1}. These values are lower than those measured at sea level in rural or industrial continental sites or in marine areas. These lower fluxes represent the net input of long-range transported OC to the ocean region whereas those measured at sea level likely reflect contributions after volatilization of those present in soils, water or local pollution sources. To this end, the isomeric composition of HCH is coincident with that observed in rural sites of central Europe (α/γ ratio 1:3). No β-HCH has been found. Comparison of the compounds present in dry only or dry + wet deposition shows the preferential association of all compounds to wet precipitation. However, when considering the annual frequency of wet deposition events, deposition associated to this precipitation mode appears to be specifically relevant for low molecular weight OC, particularly HCHs. In contrast, dry deposition seems to be responsible for a background atmospheric precipitation of similar fluxes, within a range of 10 and 65 ng m^{-2} yr^{-1}, for all compounds.

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Article 3.

INFLUENCE OF SOOT CARBON ON THE SOIL-AIR PARTITIONING OF POLYCYCLIC AROMATIC HYDROCARBONS

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Influence of Soot Carbon on the Soil−Air Partitioning of Polycyclic Aromatic Hydrocarbons

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Soil−air partitioning is one of the key processes controlling the regional and global cycling and storage of polycyclic aromatic hydrocarbons (PAHs). However, the specific processes dominating the partitioning of PAHs between these two environmental compartments still need to be elucidated. Stable and distinct atmospheric conditions paralleling different soil properties are found at Tenerife island (28°18′N, 16°29′W), which is located in permanent inversion layer conditions, and they provide interesting model cases for the study of air−soil partitioning. Analysis of phenanthrene, pyrene, fluoranthene, and chrysene showed concentrations 4- to 10-fold higher below than above the inversion layer. Similarly, soil total organic carbon (TOC) and black carbon (BC) were 11 and 3 times higher, respectively, below the inversion layer than above. The octanol−air partition coefficient (K_{OA}) derived model provides a good description of PAH soil−air partitioning coefficients (K_P) below the inversion layer but underpredicts them in the area dominated by deposition of long-range transported aerosols without inputs of organic matter from local vegetation. Inclusion of soot carbon in the soil−air partitioning model results in good agreement between predicted and measured K_P in this area but in overpredicted K_P values for the soils under the vegetation cover, which shows that the influence of soil soot carbon on PAH air−soil partitioning depends on its abundance relative to soil organic carbon. Absorption into organic matter is the dominant process in soils containing high organic carbon concentrations, whereas adsorption onto soot carbon becomes relevant in soils with low organic carbon and high soot content.

Introduction

Soil is the primary terrestrial reservoir of persistent organic pollutants (POPs) such as PAHs (*1*−*7*), and the atmosphere is their main transport vector (*8*−*11*). Soil−air exchange is therefore a key process governing the environmental fate of these compounds on a regional and global scale. Air to soil transport may occur through dry deposition of aerosols, wet deposition, or sorption to soil constituents (*12*). Soil to air diffusion is driven by the chemical potential gradient between the soil and the atmosphere. In most cases it is not clear whether soil−air partitioning is dominated by adsorption onto soil surface or absorption into the bulk soil constituents (*13*). Sorption is also dependent on temperature, relative humidity (*14*), and other soil properties such as specific surface area, particle diameter, and clay mineralogy (*15*). Nevertheless, most studies have concluded that sorption to soils is primarily controlled by partitioning into organic matter (*12*−*13*, *16*−*17*).

At equilibrium, the POP soil−air partition coefficients (K_P) for a wide range of persistent organic pollutants such as polychlorinated biphenyls are predicted from the octanol−air partition coefficients (K_{OA}; *18*−*19*). However, these studies have been focused in soils with high concentrations of organic matter, and the predictive capability of this model is limited for PAHs. The chemical and physical heterogeneity of soil organic matter and soil constituents such as soot carbon are likely additional structural parameters that influence POP sorption (*13*, *15*, *17*, *20*−*21*) but their significance is not properly evaluated with the K_{OA} model.

Soils contain different forms of carbonaceous materials. Black carbon (BC), produced by the incomplete combustion of fossil fuels and from vegetation fires, occurs ubiquitously. It can account for about half of the total organic carbon in certain soils (*22*−*23*). Structurally, BC may be essentially differentiated between soot carbon (small particle size; SC) and char/charcoal. The former originate during the condensation of hot combustion gases involving free radical reactions of acetylene species leading into PAH, macro PAH, and SC. Conversely, charcoal originates from incomplete combustion of plant tissues and diagenesis (*24*−*25*) and always contains a core of unburned biomass material (with cell structures frequently discernible).

During the past few years, the study of SC as a strong sorption matrix has received increasing attention (*22*−*32*). Adsorption onto SC has been shown to affect significantly the overall PAH sorption to sediments and aerosols (*27*−*34*) but to date its role in the soil−air PAH partitioning has not been considered. The influence of other forms of condensed organic carbon such as char/charcoal BC on air−soil partitioning also remains to be investigated. The present study is therefore devoted to assessing the sorption mechanisms driving soil−air partitioning of PAHs through the evaluation of soil−air partition models based on the octanol−air (K_{OA}) and soot−air partition coefficients (K_{SA}).

Experimental Section

Sampling. Soil samples were taken at different altitudes between 10 and 3400 m above sea level (masl) on the northern side of Tenerife Island (28°18′N, 16°29′W) which is situated in the subtropical Atlantic ocean. Soils between 10 and 2500 masl were collected with a soil corer (Lancaster University), whereas the upper soils (very stony) were sampled with a small shovel and sifted through a 500-μm sieve.

Air samples were collected at Punta del Hidalgo (47 masl) and Izaña (2367 masl). Air volumes of 80 m^3 were collected with a high-volume sampler (MCV S. A., Collbató, Catalonia, Spain) for a period of time ranging from 4 to 8 h. Aerosols were collected on glass fiber filters (GFF, Whatman International Ltd, Maidstone, England; 20.3 × 25.4 cm; 1.0 μm pore size), and gas-phase PAHs were retained on two polyurethane foam (PUF) plugs which had been previously cleaned by Soxhlet extraction with *n*-hexane. Both soil and PUFs were wrapped in aluminum foil, packed into heat-

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sealed polyester bags (Kapak corporation, Minneapolis, MN) and stored at 4 °C until analysis.

Extraction and Fractionation of PAHs in Soils. About 50 g of fresh soil was mixed with 25−50 g of anhydrous sodium sulfate for water removal. The mixtures were introduced into Whatman Soxhlet cellulose thimbles, spiked with d_{10}-benzo-[*a*]pyrene and d_{12}-benzo[*ghi*]perylene (Cambridge Isotope Lab.), and extracted with hexane/dichloromethane (4:1) for 18 h. All extracts were first concentrated by rotary vacuum evaporation to 3−5 mL and subsequently further dehydrated by elution through sodium sulfate. After rotary vacuum evaporation to ~0.5 mL, the extracts were fractionated by column chromatography using 2 g of neutral aluminum oxide. PAHs were obtained by elution with 10 mL of hexane/dichloromethane (1:2). Subsequently, the eluate was hydrolyzed overnight with KOH in methanol to remove aliphatic ester interferences. Neutral compounds were recovered with *n*-hexane and fractionated again by adsorption chromatography with aluminum oxide (2 g). After elution with hexane/dichloromethane (1:2), the PAH fraction was concentrated to 50 μL in isooctane by rotary vacuum evaporation followed by a gentle stream of purified N_2.

Extraction and Fractionation of Gas-Phase PAHs. PUFs were spiked with d_{10}-anthracene, d_{10}-benzo[*a*]pyrene, and d_{12}-benzo[*ghi*]perylene immediately after sampling to check for losses during transport and analysis. The two plugs were Soxhlet extracted in *n*-hexane for 24 h. The extracts were vacuum evaporated until 1 mL. Samples and blanks were cleaned up by adsorption on 2 g of neutral aluminum oxide. PAHs were obtained by elution with 7 mL of hexane/dichloromethane (1:2). The collected fraction was vacuum evaporated to 1 mL and then further concentrated to 50 μL under a gentle stream of nitrogen.

Instrumental Analysis. The internal standards tetrachloronaphthalene and octachloronaphthalene (L. D. Ehrenstorfer) were added to the vials prior to injection. The samples were injected into a gas chromatograph equipped with a mass selective detector (Fisons 8000 Series, Mass Selective Detector 800 Series). A fused silica capillary column (HP-5: 30 m long, 0.25 mm i.d, 0.25 μm film thickness) was used. The oven temperature program started at 90 °C (1 min hold), followed by a 4°/min ramp up to 300 °C (15 min hold). Injector and detector temperatures were 280 and 350 °C, respectively. Helium was used as carrier gas (3 mL/min). The molecular weight mass fragments of the individual PAHs were used for identification and quantification. Quantification was performed by combination of the external standard (EPA, Mix 9, L. D. Ehrenstorfer) and retention index methods. Calibration curves (detector response vs amount injected) were performed for each PAH. The range of linearity of the detector was evaluated from the curves generated by representation of detector signal/amount injected vs amount injected. All measurements were performed in the ranges of linearity found for each compound. The quantitative data were corrected for surrogate recoveries.

Total Organic Content (TOC) and Black Carbon (BC). TOC was measured by flash combustion at 1025 °C followed by thermal conductivity detection in a CHNS elemental analyzer EA1108 (detection limit 0.1%). BC was determined by the chemothermal oxidation (CTO) method (*24, 27*) (detection limit 4 μg of C). In the present paper BC refers to the measurements with this CTO method, and SC refers to soot carbon (as defined above) which in some cases may be similar to the BC measurements.

Quality Control and Assurance. Field blanks were inserted between the air samples for monitoring for possible contamination during transport and processing. They were treated and analyzed as regular samples and constituted about 30% of total samples analyzed. Fluoranthene and pyrene concentrations in blanks were in the range of 0.2−6% of sample concentration, whereas blank phenanthrene and chrysene + triphenylene concentrations were in the range of 1.6−13% of sample concentrations. For each batch of samples and blanks, sample concentrations were handled after subtraction of blank levels. Average recoveries of d_{10}-anthracene and d_{10}-pyrene for gas-phase PAH were 82 and 107%, respectively. Detection limits (determined as three times the standard deviation of the chromatographic noise near the PAH peaks) ranged between 0.025 pg/m^3 and 2 pg/m^3. PUF breakthrough was determined by injection of a mixture of phenanthrene, fluoranthene, pyrene, and chrysene + triphenylene into the first PUF plug before sampling. Replication of this test on four occasions did not show any traces of pyrene and chrysene + triphenylene in the second PUF plug and the levels of phenanthrene and fluoranthene were 7 and 6% of those in the first plug, respectively.

Negative bias in gas-phase determination may occur by PAH adsorption to filters during sampling. A recent rigorous examination of this sampling artifact showed that for sufficient sampling volume the measured gas-phase concentrations of the more volatile PAHs are close to the real values (*35*). In the present study, the measured sample volumes were 80 m^3 which corresponds to errors lower than 10% for the gas-phase concentrations of the compounds of interest.

Analysis of procedural blanks was performed with each set of nine soil samples to check for possible impurities. Replicate analysis gave dispersions lower than 15% and detection limits between 2 and 8 pg/g for soil PAH concentrations. Recoveries of d_{10}-benzo[*a*]pyrene and d_{12}-benzo[*ghi*]perylene spiked in soils averaged 66 and 82%, respectively.

The CTO method has been thoroughly tested with a wide range of potentially interfering substances and with ancillary environmental data (*24, 27*). Although there may be limitations in high-organic/low-BC matrices such as peat and plankton, the method has been demonstrated to return geochemically and isotopically consistent results for coastal sediments and aerosol particles (*24, 27, 36, 37*).

Results and Discussion

Atmospheric Conditions. The volcanic mountain system in the subtropical Atlantic Ocean is characterized by a yearly stable temperature inversion that separates air masses of lower altitude (0−1000 masl) from the free troposphere (above 1800 m). These atmospheric conditions result from the descent branch of the Hadley cell at this latitude. On the northern side of Tenerife, the atmospheric inversion layer is further enforced by a strong humidity inversion due to the influence of a wet northeastern air mass (trade winds). The combination of these two factors leads to the formation of low stratus clouds and the stabilization of two independent air masses year-round. This atmospheric structure has led to the formation of two different soil types. Entisoils predominate above the inversion layer constituting practically not-developed soils with low TOC and water content. Andisoils are the dominant form below the inversion layer (*38*).

The present study is focused in these two well-defined environments, below (0−800 masl) and above (more than 1800 masl) the inversion layer, because the atmospheric conditions are more stable and better characterized at these two altitude ranges.

Occurrence of Soil and Gas-Phase PAHs. The major gas-phase PAHs encompass naphthalene, fluorene, phenanthrene, fluoranthene, and pyrene (*39−40*). Among these, the present study is focused on the compounds currently found in higher concentration in soils, e.g., phenanthrene, fluoranthene, and pyrene. For comparison, chrysene + triphenylene is also considered. Furthermore, K_{OA} and K_{SA} values for these compounds are known (*31, 41*).

TABLE 1. Mean and Range (in parentheses) Soil and Gas-Phase PAH Concentrations, Soil Total Organic Carbon (f_{TOC}), and Soil Black Carbon (f_{BC}) Concentrations Below (BIL) and Above (AIL) the Atmospheric Inversion Layer

	BIL (0−800 masl)		AIL (1800−3400 masl)	
	soil[a] (n = 12)	gas phase[b] (n = 4)	soil (n = 26)	gas phase (n = 12)
sampling mean temperature (°C)	26	20	16	16
phenantrene (Phe)	0.81 (0.01−3.0)	980 (270−6000)	0.97 (0.03−6.8)	63 (35−150)
fluoranthene (Fla)	120 (0.03−1400)	830 (37−3600)	7.2 (0.17−130)	24 (2.9−25)
pyrene (Pyr)	10 (0.01−75)	350 (28−1400)	2.4 (0.10−23)	23 (1.4−21)
chrysene + triphenylene (C+T)	83 (0.05−1000)	54 (16−70)	24 (0.02−500)	16 (3.5−25)
f_{BC} ($\times 10^3$ g/g dw)	0.76 (0.19−2.4)		0.25 (0.06−0.91)	
predicted f_{sc} ($\times 10^3$ g/g dw)[c]	0.03 (0.01−0.09)		0.01 (0.002−0.04)	
f_{TOC} ($\times 10^3$ g/g dw)	29 (3.3−74)		2.6 (0.46−15)	
f_{BC}/f_{TOC}	0.03 (0.03−0.06)		0.10 (0.06−0.13)	

[a] Results for PAHs are given in ng/g dry weight. [b] Results for PAHs are given in pg/m³. [c] Assuming SC = 0.04 · BC (*43*).

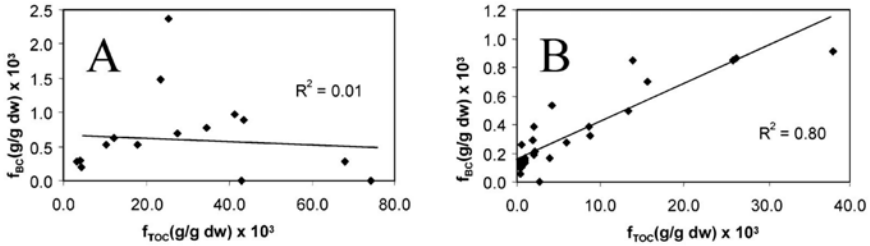

FIGURE 1. Correlation between BC concentrations and TOC in soils below (A) and above (B) Tenerife inversion layer.

Gas-phase PAH concentrations in the two vertically stratified air masses of the island are higher below the inversion layer (0−800 masl) than above it (1800−3400 masl). Measurements at Punta del Hidalgo (below inversion layer) encompass 351−11 070 pg/m³ whereas at Izaña (above inversion layer) they range between 45 and 221 pg/m³. (Table 1). The concentrations of these compounds within the inversion layer are similar to those encountered in coastal atmospheres and high-altitude sites (*31, 40*) and between 10 and 50 times lower than those found in urban areas (*31, 39*).

The differences between the two Tenerife soils are also reflected in PAH concentrations being higher below (0.1−2474 ng/g dw) than above the atmospheric inversion layer (0.3−660 ng/g dw) (Table 1). Soil PAH concentrations below the inversion layer are similar to the concentrations encountered in rural sites (*41−42*).

TOC and BC. TOC and BC concentrations, f_{TOC} and f_{BC}, respectively, are 10- to 3-fold higher, respectively, below the atmospheric inversion layer than above (Table 1). At lower altitudes there is higher variability and no significant correlation between f_{TOC} and f_{BC}. Conversely, above the inversion layer, f_{TOC} and f_{BC} show a positive significant correlation explaining 80% of the observed variability (Figure 1). This difference is consistent with the two different soils distributed vertically in the Teide Mountain.

The f_{BC}/f_{TOC} mean ratios of 0.03 and 0.10 are found below and above the inversion layer, respectively. The latter are close to those observed in aerosols of semi-rural areas (*31, 37, 44*) suggesting that deposition of aerosols may be a major BC source above the inversion layer (*45*). Thus, in these soils, BC may be predominantly SC. A correlation between f_{BC} and f_{TOC} is also commonly observed in atmospheric aerosols (*31, 44−46*) giving further support to this interpretation.

Conversely, the f_{BC}/f_{TOC} ratios below the inversion layer are in agreement with those found in soils under vegetation (0.01−0.07; *31, 37*) involving higher humic material content, and, to a lesser extent, higher char/charcoal BC. In any case, the anthropogenic activity below the inversion layer also generates SC, contributing to total BC. Fresh organic matter is therefore expected to predominate below the inversion layer and the measured BC values may contain a significant fraction of charcoal besides the anthropogenic SC. Indeed, there is no generally accepted analytical protocol and terminology for BC determination in soils. Different optical, chemical, and thermal methods are currently used. A recent comparative study (*37, 43*) for soils showed that the values measured had a wide range of variability, suggesting that the BC concept depends to a certain extent on the determination method.

Soil−Air Partitioning. The soil−air partition coefficient K_P (L/kg) is given by

$$K_P = C_S/C_G \quad (1)$$

where C_S is the individual PAH concentration in soil (pg/kg soil dry-weight) and C_G is the individual PAH concentration in the gas phase (pg/L sampled air).

Sorption to Organic Matter. The octanol−air partition coefficients have recently been useful to predict K_P values for a wide range of POPs (*18−19, 41, 47, 48*). This model is consistent with absorption into organic matter as the dominant sorption mechanism. K_P values are predicted from K_{oa} according to the following equation:

$$K_p = f_{OM}\,(\zeta_{OCT}/\zeta_{OM})(MW_{OCT}/MW_{OM}\delta_{OCT})\,K_{oa} \quad (2)$$

where f_{OM} is the fraction of organic matter in the soil (g/g soil dw), and ζ_{OCT} and ζ_{OM} are the activity coefficients of the individual PAH in octanol and soil organic matter, respectively. MW_{OCT} and MW_{OM} are the molecular weights of octanol (130 g/mol) and organic matter, respectively, and δ_{OCT} is the octanol density (0.820 kg/L, 20 °C).

Prediction of K_p values from eq 2 is limited by the lack of knowledge on ζ_{OM}, ζ_{OCT}, and MW_{OM}. Usually, the following

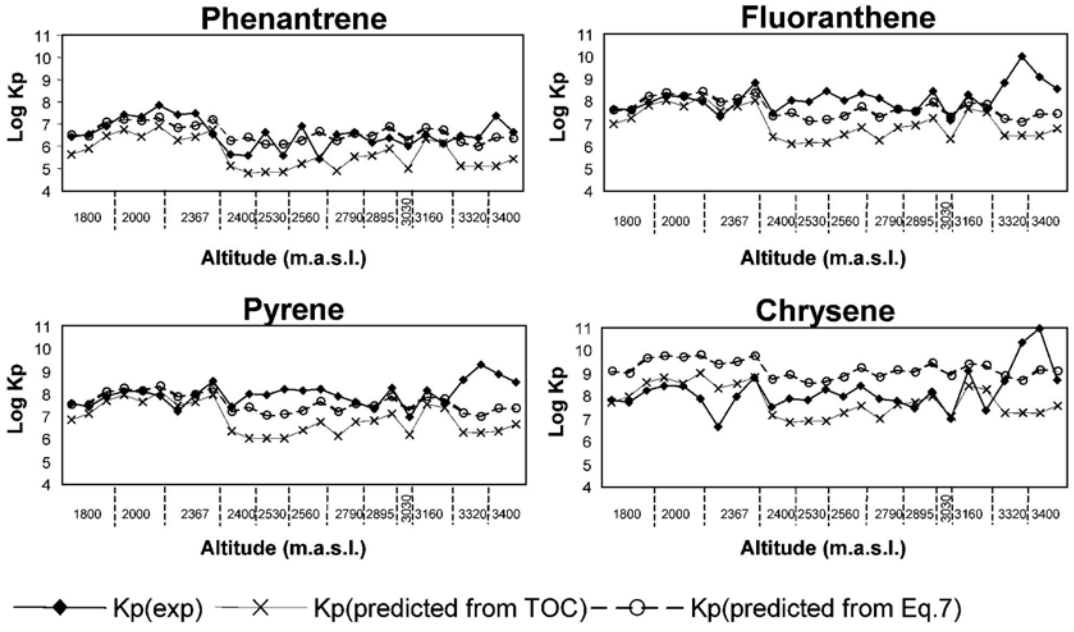

FIGURE 2. Experimental and predicted log-transformed K_p values for the soil samples collected above the inversion layer. Predicted K_p values have been estimated from TOC and eq 7 (applying SC = BC). X axis indicates altitude in meters above sea level (masl).

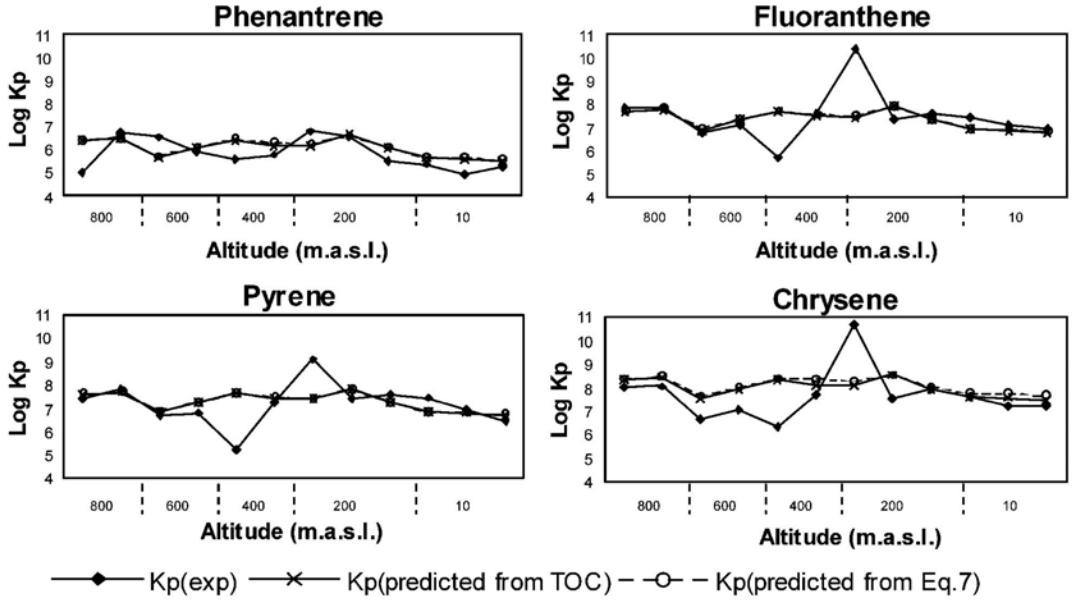

FIGURE 3. Experimental and predicted log-transformed K_p values for the soil samples collected below the inversion layer. Predicted K_p values have been estimated from TOC and eq 7 (applying SC = 0.04 BC). X axis indicates altitude in meters above sea level (masl).

assumptions are considered (*31*, *47*):

$$f_{OM} = 1.5\ f_{TOC}$$

$$(\zeta_{OCT}/\zeta_{OM})(MW_{OCT}/MW_{OM}) = 1$$

where f_{TOC} is the fraction of total organic carbon (g/g dw).

Then, K_P is given by

$$K_p = 1.5\ (f_{TOC}/\delta_{OCT})\ K_{oa} \qquad (3)$$

This absorption model has already been applied to predict K_p values for PAH gas−particle partitioning (*18*, *31*, *47*). Therefore, the K_{oa} absorption model requires knowledge of only two easily measurable parameters, K_{oa} and f_{TOC}. In the

TABLE 2. PAH Physical–Chemical Parameters and Partition Coefficients at 298K

	Log K_{OA}	Log K_{OW}[c]	Log K_{SW} (L/kg)	Log K_{SA}[f] (L/kg)
Phe	7.45[a]	4.57	6.22[d]	9.13
Fla	8.80[a]	5.22	6.96[e]	10.58
Pyr	8.43[a]	5.18	6.79[d]	10.23
C + T	10.40[b]	5.86	8.18[e]	12.27

[a] From ref (*41*). [b] Estimated from $K_{OA} = K_{OW}/H'$. [c] From ref (*49*). [d] From ref (*29*). [e] From ref (*32*). [f] Estimated from $K_{SA} = K_{SW}/H'$.

present study the K_{OA} values reported elsewhere for phenanthrene, pyrene, and fluoranthene have been used (*41*), whereas for chrysene, K_{OA} was estimated from the octanol–water partition coefficient (K_{OW}) and the dimensionless Henry's law constant (H'). The influence of temperature on K_{OA} and H has been taken into account following the procedure described elsewhere (*31*, *47*–*48*).

Figures 2 and 3 show the measured and predicted K_p values from eq 3 for samples above and below the inversion layer, respectively. Above the inversion layer, the measured K_P is underpredicted by 1 order of magnitude. A paired t test has confirmed the significance of the differences between predicted and measured K_P values ($p < 0.05$). Conversely, below the inversion layer, predictions of K_P from K_{OA} significantly agree with the measured K_P values.

Soot Carbon Adsorption Model. The high PAH affinity for SC in sediments and aerosols has been demonstrated recently (*27*–*34*). K_p values can therefore be estimated by a soot-inclusive gas–particle partitioning model (*31*)

$$K_P = 1.5\ (f_{TOC}/\delta_{OCT})\ K_{OA} + f_{SC}\ K_{SA} \quad (4)$$

where K_{SA} and f_{SC} are the soot–air partition coefficient (L kg^{-1}) and the fraction of soot carbon in the soil (g SC/g dw), respectively.

Because of the lack of experimental K_{SA} values, these are estimated from the soot–water partition coefficient (K_{SW}, L kg^{-1}) by

$$K_{SA} = K_{SW}/H' \quad (5)$$

In the present study, the K_{SW} values reported by Gustafsson (*29*) and Jonker and Koelmans (*32*) are used.

On the other hand, there is uncertainty with the estimation of f_{SC} from BC measurements for soils rich in organic matter (*24*, *43*), as the latter may include the contribution of different forms of condensed carbon such as SC and charcoal. Studies involving thermal oxidation with demineralization and hydrolysis for the specific measurement of SC showed that the f_{SC}/f_{BC} ratio in soils with high f_{TOC} (0.025–0.070 g/g dw; *43*) is fairly constant and about 0.04 in most cases. This suggests that a tentative general assumption of a f_{SC}/f_{BC} ratio equal to 0.04 may be considered for these soil types. However, this may not be true for soils with low f_{TOC} concentrations as those above the inversion layer. Recent work by Gustafsson et al. (*24*) has shown that in low f_{TOC} soils the chemothermal oxidation method provides direct f_{SC} values. In this respect, the linear correlation between f_{BC} and f_{TOC} above the inversion layer and the high f_{BC}/f_{TOC} ratios in these soils suggest that BC may be predominantly SC for these samples. In the present study, the soot-inclusive model is tested under two different potential scenarios: the first, that BC measurements are representative of real SC concentrations ($f_{SC} = f_{BC}$), and, second, that f_{SC} is only 4% of f_{BC} ($f_{SC} = 0.04\ f_{BC}$).

The K_P values predicted with the SC model outlined in eq 4 are shown in Figures 2 and 3. Above the inversion layer, the soot-inclusive model using the measured BC concentrations predicts the measured K_P values within a factor of 3 (see Table 3) and differences between measured and predicted K_P are not significant for most PAHs. This provides evidence that adsorption onto soil soot carbon controls the soil–air partitioning of PAHs above the atmospheric inversion layer. However, predictions of K_P using the estimated SC concentrations from SC/BC = 0.04 underpredict the measured K_P values. Therefore, for the soils above the inversion layer with low TOC concentrations, the measured BC concentrations are representative of the real soot carbon content. Conversely, below the inversion layer, the soot-inclusive model using the BC concentrations does not improve the model predictions — on the contrary, it overpredicts the measured K_P values. However, in this case, the use of estimated SC (SC/BC = 0.04) also provides accurate predictions, even though in this case it has virtually no influence on the predicted K_P because of the low SC concentrations. Therefore, below the inversion layer, the high concentration of organic carbon dominates the soil–air partitioning of PAHs. Another reason for the apparent lack of influence of SC in rich soils may be that the high concentrations of fresh organic matter may hinder the soot carbon fraction which may not be available to gas-phase PAHs.

Dominant Soil–Air Partitioning Mechanism. As discussed above, the dominant mechanism of PAH soil–air partitioning depends on soil characteristics. Having in mind the assumptions reported above for molecular mass of organic matter and activity coefficients in octanol and organic matter, the ratio $f_{SC}K_{SA}\delta_{OCT}/f_{OM}K_{OA}$ has been proposed to determine the dominant gas-particle partitioning (*31*). Absorption into organic matter is the dominant sorption mechanism when f_{OC} is more than 2 orders of magnitude higher than f_{SC}. Indeed, this is the case of the soils located at low altitudes of Tenerife Island (see Table 1).

Therefore, below the atmospheric inversion layer, the high concentrations of soil organic carbon dominate the soil–air partitioning of PAHs. This may be true also in those areas with abundant vegetation or rich soils with high f_{OC} values. Furthermore, high concentrations of organic matter may cover the soot carbon content in soils and therefore it may not be always available to gas-phase compounds. In contrast, the soils situated above the inversion layer correspond to a $f_{SC}K_{SA}\delta_{OCT}/f_{OM}K_{OA}$ ratio higher than one due to relatively high f_{SC} values and therefore adsorption to soil SC is the dominant

TABLE 3. Statistical Comparison of Measured and Predicted K_p Values below (BIL) and above (AIL) the Inversion Layer at Tenerife

Compared Means[a]	mean difference (measured Log K_P − predicted Log K_P)		p-value	
Log K_p (exp) vs.	BIL	AIL	BIL	AIL
Log K_p (predicted from eq 3)	−0.07	1.03	0.63	<0.00001
Log K_p (predicted from eq 4[b])	−0.66	0.26	<0.0001	0.03
Log K_p (predicted from eq 4[c])	−0.12	0.93	0.39	<0.0001

[a] Compared means correspond to all the available data from Phe, Fla, Pyr, and C + T. The t test for paired samples was conducted at $p < 0.05$ (95% confidence level). [b] SC = 0.04 · BC. [c] SC = BC.

process. Generalizing, this will be the scenario also for soils poor in organic matter that are receptive of deposited aerosols.

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Article 4.

ATMOSPHERIC SEMI-VOLATILE ORGANOCHLORINE COMPOUNDS IN EUROPEAN HIGH MOUNTIAN AREAS (CENTRAL PYRENEES AND HIGH TATRAS)

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Atmospheric semi-volatile organochlorine compounds in European high mountain areas (Central Pyrenees and High Tatras)

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Abstract

Atmospheric samples from two European high mountain areas showed similar composition of semi-volatile organochlorine compounds (SOC). Nearly all compounds were predominantly found in the gas phase and only the less volatile such as some polychlorobiphenyls (PCB), e.g. #149, #118, #153, #138 and #180, were found in higher abundance in the particulate phase. Hexachlorobenzene, 49-85 pg m^{-3}, is the dominant SOC. This compound is only found in the gas phase being well distributed through the troposphere and showing a uniform composition irrespective of season. SOC of present use, like hexachlorocyclohexanes and endosulfans, were found in higher concentrations in the warm periods, 32-46 pg m^{-3} and 4-10 pg m^{-3} in the gas+particulate phase, respectively, reflecting their seasonal pattern of use in many European countries. PCB and 4,4´-DDE, 39-42 pg m^{-3} and 4-6 pg m^{-3} in the gas+particulate phase, respectively, also showed a seasonal trend despite they are not manufactured and their use has been drastically restricted since the eighties. The seasonal differences mainly reflect a higher occurrence of air masses with strong continental inputs in the warm than in the cold periods. In this respect air

masses travelling at the high troposphere (backwards air mass trajectories > 6000 m) have been observed to carry considerably smaller PCB and 4,4'-DDE loads (9.3±2.8 pg m^{-3} and 0.4±0.05 pg m^{-3}, respectively) than average.

Introduction

Studies in the past decade have shown the presence of organochlorine compounds in considerable amounts in atmospheric deposition, soils, lake waters, sediments, and fish from European (1-3), African (4, 5) and North American (6, 7) high mountain sites. These areas are situated above the local tree line, far away from pollution sources or direct impact of human activity, and receive the pollutants resistant to long-range atmospheric transport (LRAT) (8).

Several semi-volatile organochlorine compounds (SOC) are included in this LRAT group due to their chemical stability vs degradation. Between the thirties and eighties these compounds were produced and used in large quantities for agricultural and industrial purposes in the mid- and low latitudes of the Northern Hemisphere (9). Due to their toxic effects in wildlife and humans, the production and use most SOC compounds, like DDTs, hexachlorobenzene (HCB), polychlorobiphenyls (PCB) and technical hexachlorocyclohexane (HCH; including the α, β and δ isomers besides the active γ isomer), were severely restricted or prohibited which resulted in strong emission decreases, e.g. in the order of 90% for PCB (9). However, nowadays some amounts are still incorporated into the environment as consequence of accidental release and/or their presence in products or equipment of current use (9) and they may cause deleterious effects (10, 11). Other SOC, such as pure γ-HCH, are restricted to uses in non aerial applications such as soil and seed treatment, veterinarian and human insecticide, indoor, etc. (12) and others, e.g. endosulfan, are still used in agriculture.

The differences in physico-chemical properties of the individual SOCs, like vapour-pressure and solubility, in combination to meteorological conditions give rise to their fractionation and selective trapping during transport and deposition in remote areas (13-14). Studies in European high-mountain lake sediments and fish showed that a selective trapping effect is also occurring in these areas (3), where a significant positive correlation was found between less volatile organochlorine compounds (vapour pressure < 10^{-5} Pa) and altitude. Higher concentrations were found at higher altitude. However, no correlation was observed for the more volatile compounds (vapour pressure > 10^{-5} Pa).

The occurrence of these pollutants in high mountain areas requires a better understanding on the mechanisms involved in their atmospheric transport. For this purpose, atmospheric gas and particulate phase samples were collected in the Central Pyrenees (Catalonia, Spain) and the High Tatras (Republic of Slovakia) (Figure 1). The first mountain range is situated in the periphery of the European continent and the second in central Europe. Atmosphere in the Central Pyrenees was sampled near the lake Estany Redon (42°38´33.5´´N; 0°46´12.7´´E; 2240m) and in the High Tatras

near the lake Skalnaté Pleso (49º06´36´´N; 20º08´24´´E; 1778m). PCBs, HCB, HCHs, endosulfans and DDTs were analyzed in the samples. Meteorological data and atmospheric back-trajectories were obtained corresponding to each sampling date. To the best of our knowledge this is the first report on the SOC composition in the atmosphere of European high mountain areas.

Methods and Materials

Sample Collection, extraction and analysis. Sampling and analytical procedures were described elsewhere (4). Briefly, samples were collected with a high volume device (HVS) (MCV, S.A., Collbato, Catalonia, Spain) consisting of a pump equipped with two polyurethane foams (PUFs) and a glass fiber filter (GFFs).

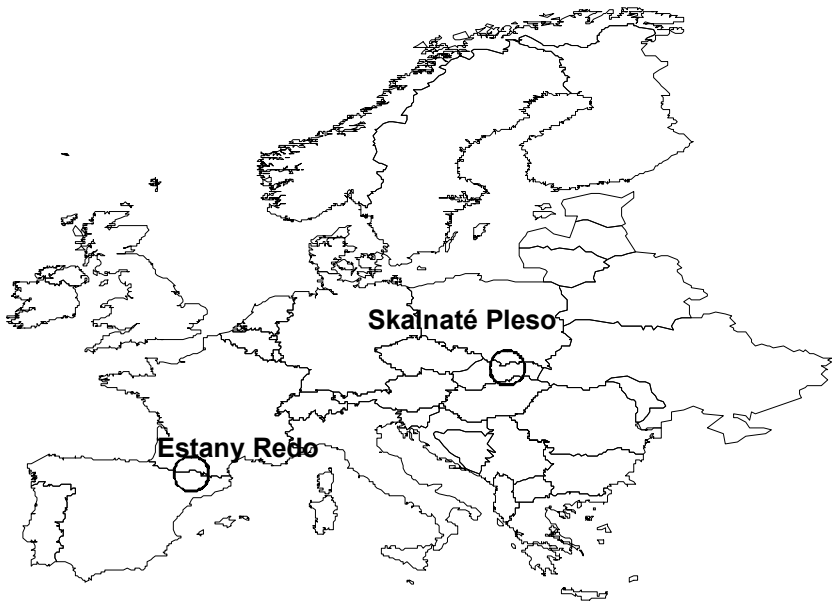

Figure 1. Atmospheric sample site in the Central Pyrenees (Estany Redon) and the High Tatras (Skalnaté Pleso).

Collected sample volumes were between 120 m^3 and 280 m^3. Field blanks were obtained by installing PUF and GFF in the HiVols and leaving them there for 6 hours without running the pump. After sampling PUFs and GFFs and their blank equivalents were stored below 0ºC and transported to the laboratory.

PUFs and GFFs were Soxhlet extracted for 24h in hexane and hexane:dichloromethane (DCM) (4:1 v/v), respectively. The extracts were concentrated to 1 ml by vacuum rotary evaporation and then cleaned-up by adsorption chromatography on a column packed with 2 g of aluminium-oxide (Fluka Type 507C, Fluka AG, Switzerland) and elution with 8 mL of hexane:DCM (1:2 v/v). They were then concentrated in iso-octane (Merck, Darmstadt, Germany)

until 50µl. Before instrumental analysis tetrachloronaphthalene was added to the vials for correction of possible small differences in injection volume or dilution.

The extracts were injected into a gas chromatograph equipped with an electron capture detector (GC-ECD) for the analysis of HCB, PCB congeners #18, #28, #52, #101, #110, #149, #118, #153, #138, #180 and DDTs (4,4´-DDE and 4,4´-DDT). HCHs (α-HCH and γ-HCH) and endosulfans (α-endosulfan and β-endosulfan) were analysed on a gas chromatograph coupled to a mass spectrometer with negative ion chemical ionisation (GC-MS-NICI). A Fisons MD 800 instrument (quadrupole-detector, THERMO Instruments, Manchester, UK) was used. Both instruments were equipped with a capillary column HP5-MS (30 m x 0.25 mm i.d. x 0.25 µm film thickness). Helium was used as carrier gas (1.1 mL min^{-1}). The oven temperatures were programmed from 90ºC (1 min) to 120ºC at 15ºC min^{-1} and then to 300ºC at 4ºC min^{-1} with a final holding time of 10 min. Samples were injected in split/splitless mode at 280ºC in both instruments. In the GC-MS-NICI, ion source and transfer line temperatures were 150ºC and 280ºC, respectively. Ammonia was used as reagent gas. Ion source pressure (currently 1.6 Torr) was adjusted to maximize the perfluorotributylamine ions (m/z 312, 452, 633, and 671). Ion repeller was 1.5 V. Data were acquired in selected ion monitoring mode with dwell time of 0.06 s and span of 0.10 amu. The ions selected for α-HCH and γ-HCH were m/z 71 and 255, respectively. α-Endosulfan and β-endosulfan were quantified with m/z 406 and 272, respectively (15).

Quality Control and Assurance. PUF breakthrough was determined by injection of PCB congeners #40, #155 and #185 into the first PUF, transport to the field and adsorption of 300 m^3 with the HVS. All congeners were present in the first PUF and no traces of these standards were observed in the second PUF plug after this test. LODs (determined as three times the standard deviation of the chromatographic noise near the peaks of the analysed compounds) were 0.04-0.23, 0.03, 0.20, 0.08, 0.12-0.15 and 0.05-0.11 pg m^{-3} for PCBs, HCB, 4,4´-DDE, 4,4´-DDT, HCHs and endosulfans, respectively. Field blanks for PUF and GFF were collected in all sampling periods as described above for control of possible contamination during transport and processing. These blanks were treated and analysed as regular samples and substracted from the sample concentrations. PUFs field blank values were below limit of detection (LOD) for HCB, HCHs, endosulfans, 4,4´-DDT and PCB#180, in the range of 1-10% sample concentrations for 4,4-DDE, PCB#18, and PCB#28 (ca. 0.25 pg m^{-3}), between 10-20% for PCB#52, PCB#101, PCB#110 and PCB#149 (ca. 0.7 pg m^{-3}) and 20-30% for PCB#118, PCB#153, and PCB#138 (ca. 0.5 pg m^{-3}). Field blank values of GFFs were below LOD for HCB, HCHs, endosulfans, 4,4'-DDT, PCB#18, PCB#28 and PCB#180 and in the range of 20-40% of sample concentrations for 4,4´-DDE, PCB#52, PCB#101, PCB#110, PCB#149, PCB#118, and PCB#153 (ca. 0.2 pg m^{-3}). Injection of PCB#30 and PCB#209 standards into the samples and blanks did not show significant losses

during transport (recoveries >81%). Average recoveries for PCB#30 and PCB#209 were 70 ± 8% and 92 ± 17% in the PUFs, respectively, and 63 ± 10% and 83 ± 16%, respectively, in the GFFs.

Temperature measurements. An automatic weather station (AWS) situated at the border of the lake Estany Redon allowed to measure air temperatures every 30 min during sampling. Compilation of these data provided mean temperature values for each sampling period. In Skalnaté Pleso the mean atmospheric temperatures for each sampling period were obtained from on line measurements of the Slovakian Meteorological Institute (SAV) which has a meteorological station at this site.

Back-trajectories. The origin and altitude of the air masses arriving to the two sample sites were calculated from back-trajectories using the HIRLAM model of the Spanish National Institute of Meteorology (INM). This model is based on isentrophic surfaces that provide a more realistic representation than those elaborated from isobaric surfaces (16-17). The calculations were performed at 0:00 UTC and 12:00 UTC for 5-days back each sampling period with 1 h step. The isentrophic surfaces for each back-trajectory at Estany Redon and Skalnaté Pleso stations were selected according to the observed potential temperature at 2240 m and 1778 m, respectively.

Results and Discussion

The data of the samples collected at each site are summarized in Table 1. In both cases they cover cold and warm seasonal periods distributed over two years (Redon) and 12 months (Skalnaté). Snow cover was present in all cases except in the samples taken in June 2001 and June 2002 at both sites.

Atmospheric concentrations. A summary of the atmospheric OC data is given in Table 1. Most SOCs were predominantly found in the gas phase, which is in agreement with the atmospheric partitioning of these compounds reported in other studies (4, 18-20). HCB is the most predominant gas phase SOC at both sample sites, followed by γ-HCH, α-HCH, 4,4´-DDE, the individual PCB congeners, namely #18, #28, #52, #101, #110 and #149, and endosulfans. 4,4´-DDT was not found in any of the samples. γ-HCH is the most predominant SOC in the particulate phase, followed by 4,4´-DDE, α-HCH, endosulfans and the less volatile PCBs. HCB and 4,4´-DDT were below detection limits in this phase.

The geometric mean HCB concentration at Skalnaté Pleso, 85 pg m^{-3} (standard deviation, s.d., 28 pg m^{-3}), is significantly higher than at Estany Redon, 49 pg m^{-3} (s.d., 19 pg m^{-3}) (ANOVA, $p<0.001$). These levels were relatively constant throughout the entire sampling period (Figure 2) indicating that the amounts of this compound arriving to both sites are relatively constant. The observed concentrations are in the same range as those found in the free-troposphere at Tenerife

Table 1. Atmospheric concentrations of the main SOC at the two mountain areas (geometric means and lower and upper levels). Mean values of other locations are given for reference.

Location and sampling dates	HCB	α HCH	γ HCH	4,4'-DDE	4,4'-DDT	α endosulfan	β endosulfan	ΣPCB	Reference
				pg/m^3					
Estany Redon (Central Pyrenees)	49 (36-98)[a]	8 (2-25)[a]	22 (5-91)[a]	3.3 (0.9-12)[a]	<LOD	2.3 (0.8-6)[a]	0.7 (0.4-1.3)[a]	34 (16-70)[a,c]	This study
(27-29Nov00, 11-12May 01, 4-5Feb02, 25Mar02, 17-18Jun02, 14Jan03; n =20)	<LOD[b]	0.3 (LOD-1.9)[b]	1.9 (0.4-10.1)[b]	0.3 (0.2-0.6)[b]		0.4 (0.2-0.6)[b]	0.2 (0.1-0.3)[b]	5.5 (3.5-8.8)[b,c]	
Skalnaté Pleso (High Tatras)	85 (62-119)[a]	15 (34-7)[a]	30 (11-86)[a]	5 (2-12)[a]	<LOD	7 (1.3-42)[a]	2.3 (0.5-7)[a]	38 (23-64)[a,c]	This study
(29-30Jun01, 20-22Sep01, 19-20Dec2001, 27Mar02, 16-17Jun02; n =10)	<LOD [b]	0.2 (0.1-0.5)[b]	0.8 (0.3-2.2)[b]	0.8 (0.5-1.2)[b]		0.3 (0.1-0.8)[b]	0.3 (0.2-0.5)[b]	4.0 (2.9-5)[b,c]	
OTHER LOCATIONS (gas + particulate phase)									
Tenerife 2367 m[e] (sampling period 1999-2000)	51	6	11	4	1			78[c]	(4)
Tenerife 47 m[e] (1999-2000)	72	22	26	22	10			190[c]	(4)
North Atlantic (1989-1990)		200	66	3	4			290[d]	(27)
Bermuda 3000 m[e] (1986)	98	300	16					160[d]	(21)
Bermuda 500 m[e] (1986)	89	120	43					330[d]	(21)
Spitsbergen (1992)	205	140	32					13[c]	(22)
Spitsbergen (1993)	92	77	14	0.29	0.26				(39)
Alert (1993-1994)	56	60	11	0.45	0.14	4.2[f]			(28)
Tagish (1993-1994)	48	79	12	0.53	0.19	7.0[f]			(28)
Dunai (1993)	55	40	9.8	0.36	0.14	3.0[f]			(28)
Eastern Arctic Ocean (1996)		37	17						(29)
Lake Baikal (1991)	190	490	105	8	8			89[c]	(23)
Swedish west coast (1996)								40[c]	(26)
Rural UK (1992-1999)								38[c]	(25)
Senga Bay (1997-1998)	11	9.4	25	<LOD	12	24			(30)

[a]gas phase. [b]particulate phase. [c]sum of PCB18, 28, 52, 101, 110, 149, 118, 153, 138, 180. [d]no data on individual congeners. [e]meters above sea level. [f]total endosulfans

Table 2. Linear regression model of the natural logarithmic gas phase SOC concentrations versus the reciprocal of the absolute temperature.

	Estany Redon					Skalnaté Pleso				
	R^2	sig p	S	Δ H (kJ/mol)	95%int.error	R^2	sig p	S	Δ H (kJ/mol)	95%int.error
HCB	0.06	0.314	-1427			0.15	0.265	-1028		
α-HCH	0.07	0.265	-5812			0.66	**0.004**	-5173	-43	±25
γ-HCH	0.20	**0.048**	-11711	-97	±96	0.73	**0.002**	-7227	-60	±30
α-endosulfan	0.13	0.117	-6861			0.68	**0.003**	-11528	-96	±54
β-endosulfan	0.25	**0.025**	-5821	-48	±41	0.66	**0.004**	-8626	-72	±42
4,4´-DDE	0.32	**0.009**	-13294	-111	±79	0.84	**0.000**	-6565	-55	±19
PCB18	0.14	0.105	-7111			0.38	0.057	-2605		
PCB28	0.30	**0.012**	-9043	-75	±59	0.29	0.107	-3432		
PCB52	0.32	**0.010**	-8470	-70	±51	0.52	**0.019**	-3265	-27	±21
PCB101	0.36	**0.005**	-6980	-58	±38	0.83	**0.000**	-4381	-36	±13
PCB110	0.28	**0.015**	-9300	-77	±61	0.53	**0.017**	-3187	-26	±20
PCB149	0.43	**0.002**	-12740	-106	±60	0.77	**0.001**	-3981	-33	±15
PCB118	0.35	**0.006**	-10580	-88	±60	0.55	**0.014**	-3726	-31	±23
PCB153	0.52	**0.0001**	-10421	-87	±41	0.78	**0.001**	-5291	-44	±19
PCB138	0.23	**0.032**	-5914	-49	±44	0.79	**0.001**	-4285	-36	±15
PCB180	0.30	**0.012**	-6356	-53	±40	0.76	**0.001**	-4159	-35	±16

and Bermuda, 98 pg m^{-3} and 51 pg m^{-3}, respectively (4, 21). They are lower than those at Spitsbergen or Lake Baikal, 205 pg m^{-3} and 190 pg m^{-3}, respectively (22-23).

The measured PCB congener profiles in the two sample sites are very similar showing a rather homogeneous congener distribution except for PCB#18 and #28 that are present in much lower abundance (Figure 3). The gas phase PCB congener distributions are less uniform being predominated by PCB#52 and #101. PCB#18 and #28 are in higher abundances in the gas than in the particulate phase. The less volatile compounds, such as PCB#149, #118, #153, #138 and #180, are less abundant in the gas than in the particulate phases. These results are consistent with previously reported gas-particulate phase distributions (24).

The gas phase PCB concentrations are very similar in the two sites (geometric means of the sum of all analyzed congeners 34 pg·m^{-3} and 38 pg·m^{-3} at Estany Redo and Skalnaté Pleso, respectively). PCB#52 and #101 are the most abundant congeners in both sites. PCB#18 shows slightly higher concentrations at Estany Redon. The distributions found in this study are also similar to those found in the free-troposphere at other sites, e.g. at Tenerife (4) and in the same range as those found in Temperate areas such as Stoke Ferry, High Muffles or Hazelrigg (UK) (35-46 pg m^{-3} (25)) or in the Swedish West Coast (40 pg m^{-3} (26)). However, they are higher than those found in at high latitudes, e.g. Pallas (Findland), 11 pg m^{-3} (not published) and Svalbard, 10 pg m^{-3} (23).

Similar gas phase concentrations of 4,4'-DDE at Estany Redon and Skalnaté Pleso are found, with geometric means of 3.3 pg m^{-3} and 5 pg m^{-3}, respectively. They are in the same range as those in remote areas of the Northern Atlantic or in the free troposphere (Tenerife), 3 pg m^{-3} and 4 pg m^{-3}, respectively (4, 27). Again, they are higher than those reported in Arctic sites such as Alert (Canada), 0.1-0.21 pg m^{-3} or Alesund (Europe), 0.29-1.9 pg m^{-3} (28). In all atmospheric samples, 4,4'-DDE is detected while 4,4'-DDT was below LOD indicating that the inputs of this pesticide correspond to aged mixtures and not to recent emissions.

HCHs are predominantly found in the gas phase (Table 1). γ-HCH is the isomer with highest individual concentration at both sites. The concentrations are highest in May 2001 at Estany Redon with geometric mean values of 204 pg m^{-3}. At Skalnaté Pleso the highest geometric mean values, 93 pg m^{-3}, were observed in June 2001. The geometric mean values for the entire sampling periods at Estany Redon and Skalnaté Pleso were 22 pg m^{-3} and 30 pg m^{-3}, respectively. These values are similar to those found in the atmosphere of the Northern Atlantic and Spitsbergen, 11-66 pg m^{-3} (4, 21, 22, 27) or in the Arctic Ocean (29). α-HCH was found at concentrations of 8 pg m^{-3} and 15 pg m^{-3} at Estany Redon and Skalnaté Pleso, respectively, being similar to those found at Tenerife (6 – 22 pg m^{-3}; 4) but lower than those found in the Arctic Ocean (37 pg m^{-3}; 29) in Spitsbergen (140 pg m^{-3}; 22) or in Bermuda (120-300 pg m^{-3}; 21). The observed $\alpha/(\alpha+\gamma)$ gas phase average ratios at Estany Redon and Skalnaté Pleso, 0.27 ± 0.13 and 0.34 ± 0.08, respectively, reflect direct inputs of the γ- isomer that is still used for agriculture purposes. HCH mixtures from remote marine sites are dominated by the α- isomer resulting in $\alpha/(\alpha+\gamma)$ ratios higher than 0.5.

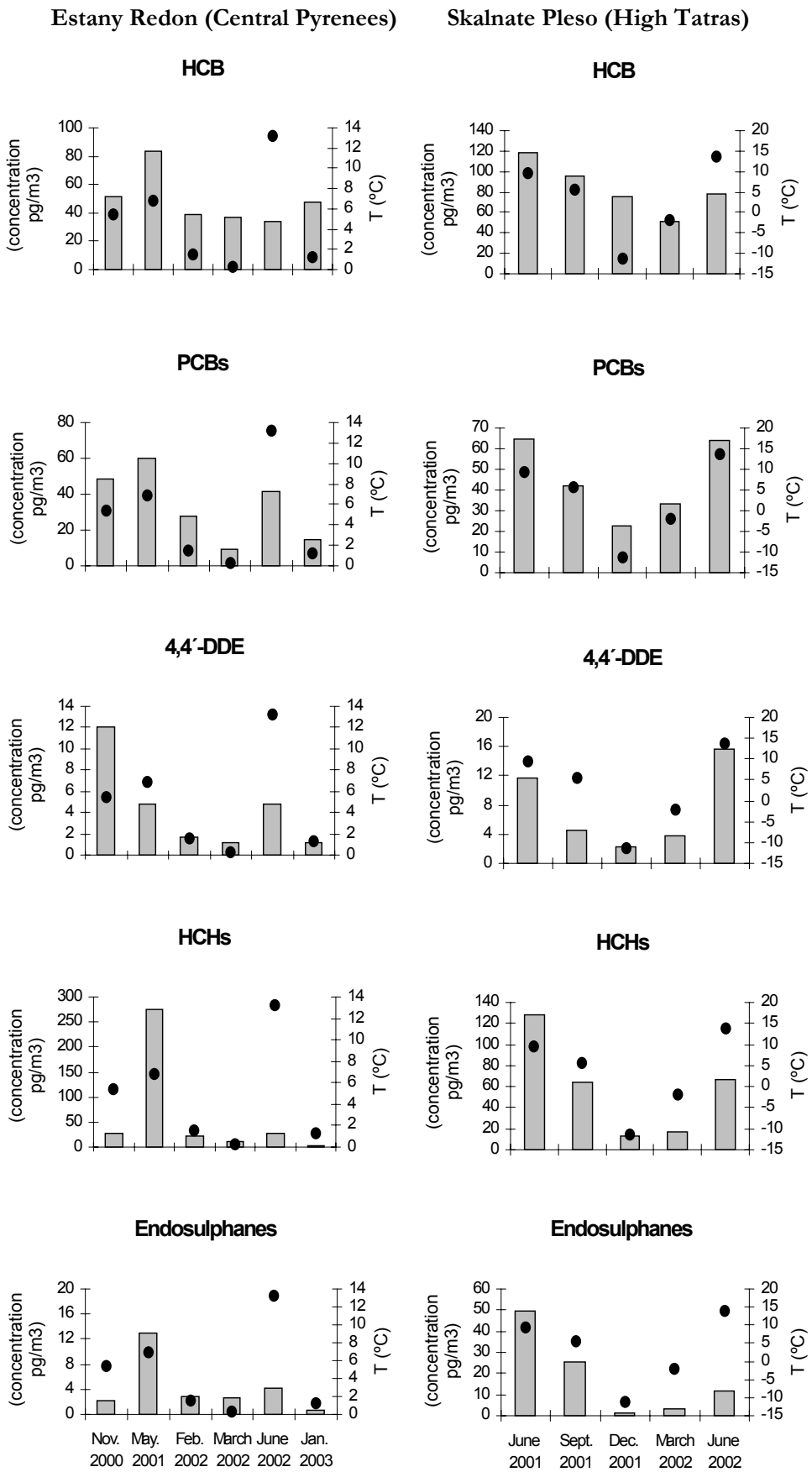

Figure 2. Geometric means of gas phase SOC in different sampling periods (bars) and the average ambient temperature (dots).

The α-endosulfan/(α-endosulfan+β-endosulfan) ratio observed in the samples from Estany Redon and Skalnaté Pleso, 0.73 ± 0.12 and 0.76 ± 0.11, respectively, are very similar to the ratios of technical endosulfan used in agriculture. Skalnaté Pleso shows significantly higher gas phase concentrations of endosulfans than Estany Redon, with geometric means of 7 pg m^{-3} and 2.3 pg m^{-3} respectively (ANOVA, $p<0.05$). They are mainly present in the gas phase (Table 1) as observed in previous studies (30). α-endosulfan levels are in the same range as the concentrations found in remote sites such as the Arctic, 0.04-3.4 pg m^{-3} (28) or Senga Bay, 0-61 pg m^{-3} (31)

Seasonal patterns and temperature dependence. The temperature intervals represented by the sampling periods of Estany Redon and Skalnaté Pleso are 14ºC (-1ºC – 13ºC) and 25ºC (-11ºC – 14ºC), respectively. A rough examination of the average concentrations in these two sites evidences a parallelism between the atmospheric concentrations of most SOCs and ambient temperature differences (Figure 2). Both at Estany Redon and Skalnaté Pleso linear regression of the natural logarithm of the gas phase SOC concentrations versus the reciprocal of absolute temperature (22, 31-33) shows a significant correlation for all SOCs with vapour pressure lower than $10^{-1.8}$ Pa (Table 2). That is, 4,4'-DDE, PCB#52 and the more chlorinated congeners. In contrast, HCB and PCB#18 do not show any temperature dependence. The differences are due to more uniform concentrations of the compounds with higher vapour pressure round the year (Figure 2). The correlation coefficients (r^2) are higher in Skalnate Pleso than in Estany Redon, 0.55-0.84 and 0.20-0.52, respectively (Table 2) which is in agreement with the larger temperature span represented in the former.

HCH and endosulfans also exhibit temperature dependence despite their relative high volatility, e.g. $10^{-0.7}$-$10^{-0.92}$ Pa for HCH and $10^{-2.1}$-$10^{-2.7}$ Pa for endosulfans. All isomers are significantly correlated to reciprocal of temperature in Skalnate Pleso. γ-HCH and β-endosulfan are correlated in Estany Redon which is in agreement with the measurements of atmospheric deposition at this site, where higher levels of these SOCs were also found in the warm periods (1-2). Since these compounds are still in use, the linear dependence mainly reflects their seasonal pattern of application for crop protection purposes, involving the release of higher amounts of these pesticides during the warm periods. The lack of correlation between the atmospheric concentrations of α-HCH and temperature in Estany Redon may be caused by the ban of the technical HCH mixture which contains this isomer in significant proportion (60-70%) and was replaced by pure γ-HCH. Thus, the correlation between these compounds and reciprocal of temperature does not reflect an environmental redistribution process due to the SOC physico-chemical constants but seasonal application patterns related to human activities.

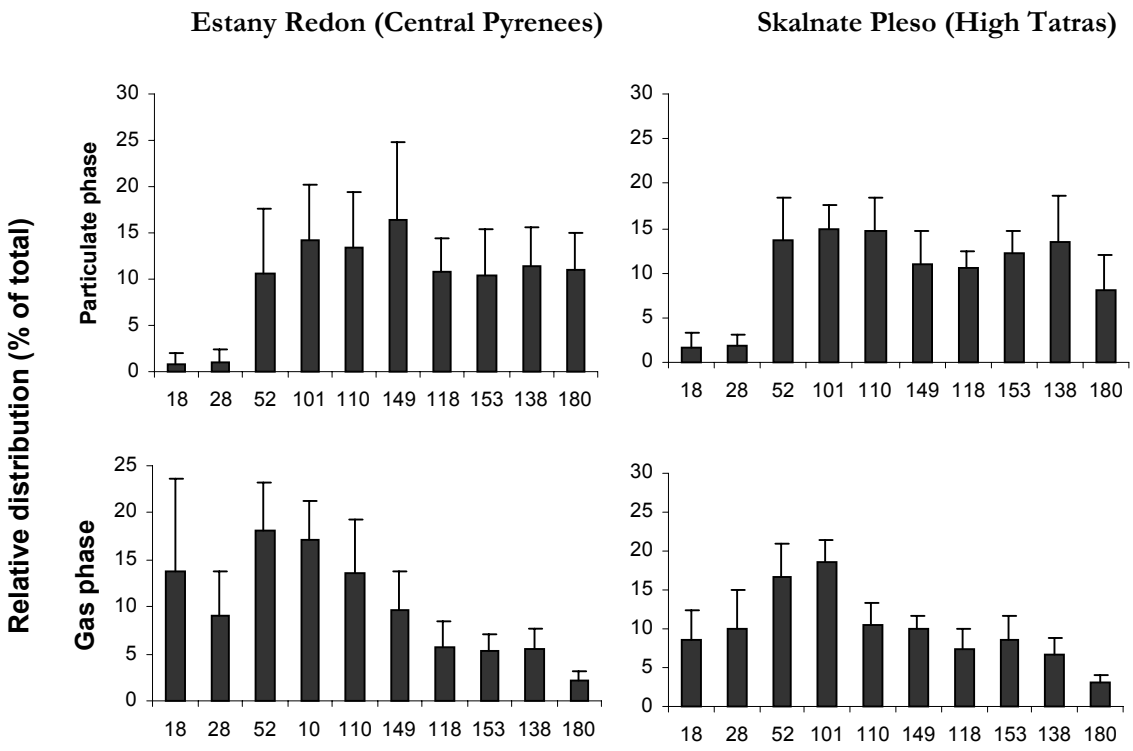

Figure 3. Relative distribution of PCB congeners in particulate and gas phase.

In a first approach, the observed temperature dependence of the less volatile compounds points to evaporation/condensation effects or solid-gas phase transfer as main factors for SOC occurrence in the gas phase. The slopes of the straight lines can be used for the calculation of the phase-change pseudo-enthalpies ($\Delta H = S\ R$, S = slope of the linear regression, R = 8.314 J K^{-1} mol^{-1}). In Skalnate Pleso, the site where highest linear correlation coefficients between gas phase concentrations and temperatures have been found, the enthalpies obtained range between 27-36 kJ mol^{-1} for the PCB and have values of 55 kJ mol^{-1} for 4,4'-DDE (Table 2). The 95% confidence errors for these enthalpies are about ±40% of the absolute values for the enthalpies obtained from linear correlations with significance $p<0.001$ (4,4'-DDE and PCB#101, 149, 153, 138 and 180) or up to ±75% for those derived from correlations with $p<0.05$ (PCB#52, 110 and 118).

The volatilization enthalpies for the PCB measured in laboratory conditions range between 70 and 97 kJ mol^{-1} (34, 35). Coincidence between laboratory and field volatilization enthalpies could indicate that the pollution sources are situated nearby since the compounds could reach the area of study rapidly after evaporation from local sources. On the contrary, when small enthalpy values are obtained from field data, e.g. field volatilization enthalpies are smaller than laboratory-measured enthalpies, LRAT has been proposed to be the main mechanism controlling the distribution of atmospheric SOC (32). Thus, the enthalpies measured at Skalnaté Pleso represent about one third of the laboratory-measured values pointing to LRAT as control mechanism.

In Estany Redon, the observed field enthalpies for PCB and 4,4'-DDE are higher than those in Skalnate Pleso being nearly coincident with the above mentioned laboratory values. However, the 95% confidence errors of these values are about ±70-80% of the slope-derived enthalpies (±47% only for PCB#153) which is consistent with the larger scatter of the curve fitted straight lines than in Skalnate Pleso (as reflected in lower r^2 values). As mentioned above, coincidence between laboratory and experimental enthalpies could be indicative of nearby pollution inputs arriving to the site of study by volatilization (32). However, this may not be always the case since there are no pollution sources nearby Estany Redon. In addition, analysis of PCB in the soils situated nearby this lake and Skalnate Pleso show about the same values or even higher concentrations in the latter, e.g. 0.41 and 0.87 ng g^{-1} in Estany Redon and Skalnate Pleso, respectively (36). Thus, assuming that the same processes are responsible for the SOC occurrence in the atmosphere of Estany Redon and Skalnate Pleso, the data from the latter explains better than the former the importance of LRAT as primary mechanism for SOC transfer to these remote mountain areas.

Back-trajectories. The air masses that arrive at Skalnate Pleso are mainly oceanic (19-20 December 2001, 20-22 September 2001, 17 June, 2002; Figure 4) or continental (29-30 June 2001, 27 March 2002, 16 June 2002; Figure 4). These two groups are characterized by well defined differences in terms of SOC composition. Thus, all PCB, 4,4'-DDE, endosulfans and HCHs (sum of isomers α and γ) are found in higher concentrations in the samples whose air package has passed longer time over the continent, 52, 8.3, 16 and 58 pg m^{-3}, respectively, than those of more oceanic origin, 31, 3.6, 6.6 and 39 pg m^{-3}, respectively (Figure 5). Only HCB shows similar concentrations in both cases, 85-87 pg m^{-3}. The higher concentrations in the continental group of air samples is consistent with emissions of pollutants from the continent since, as mentioned above, these were manufactured and used in Europe some decades ago (PCB and 4,4'-DDE) or they are still in use (HCH and endosulfans). In turn, the group of air samples from continental origin were collected at warmer average in situ temperatures than those of oceanic origin, 7.8ºC and 1.2ºC, respectively. Thus, as suggested from the low enthalpy values found in the previous section, the presence of SOC in the atmosphere of these high altitude sites may originate from LRAT. However, the source of these pollutants is mainly located in the European continent.

The air samples collected at Estany Redon do not have such well defined differences such as continental or oceanic (Figure 4). This is obviously due to the situation of the sampling site which is located on the periphery of the European continent (Figure 1). Nevertheless a group characterized by air masses of more continental origin (11-12 May 2001, 17-18 June 2002; Figure 4) can be differentiated from another of more oceanic trajectories (27-29 November 2000, 4 February 2002, 16 January 2003; Figure 4). In addition, another group of very high altitude trajectories (25 March 2002; Figure 4) has been identified. This last group is characterized by air masses travelling

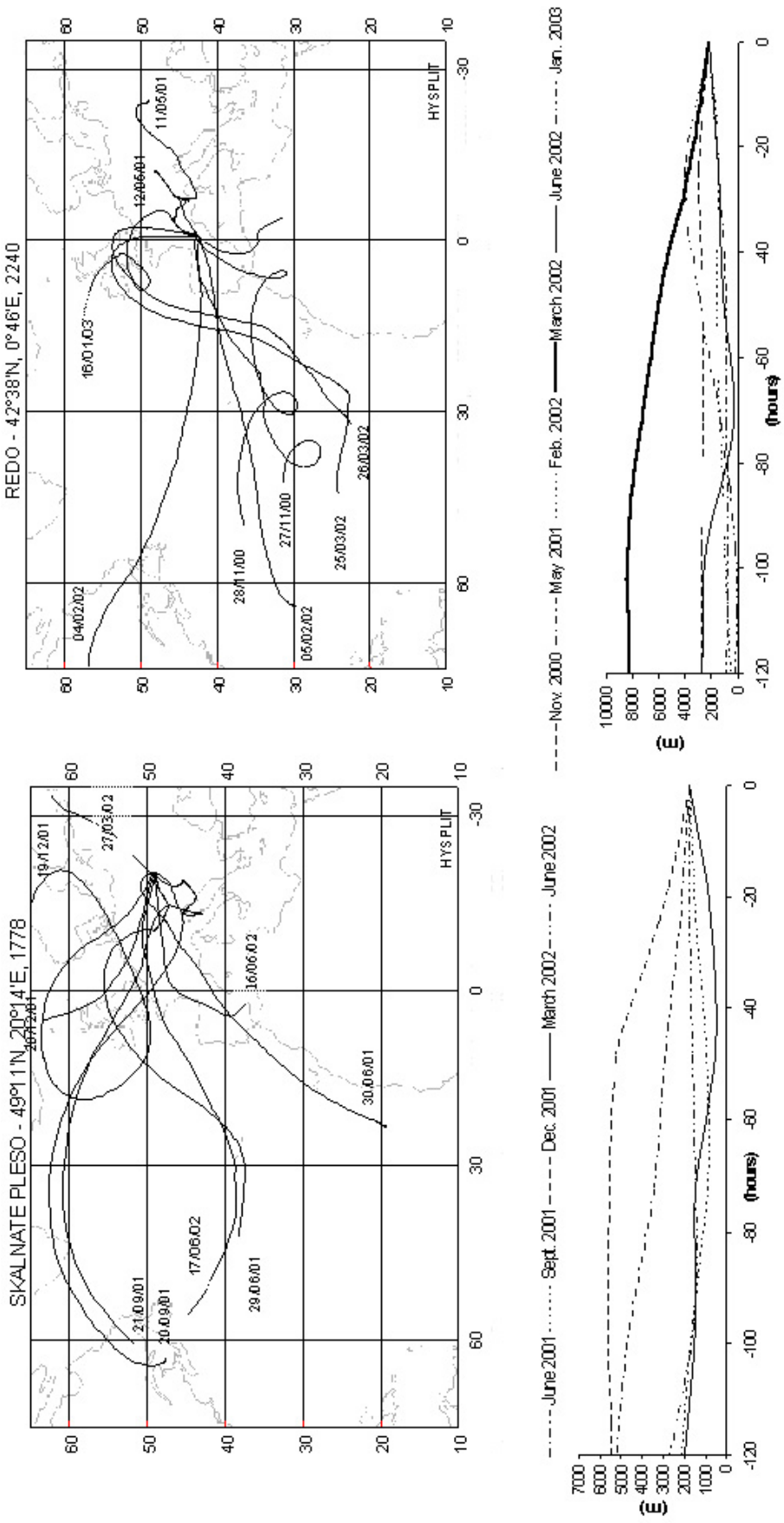

Figure 4. Back-trajectories of the Skalnaté Pleso (left) and Estany Redon (right).

over 6000 m most of the time. The sample group of more continental trajectories exhibit slightly higher geometric means for the summed PCB congeners (60 pg m^{-3}) than the group of more oceanic origin, 38 pg m^{-3}, due to the higher abundance of the lighter PCB congeners #18, #28 and #52 in the samples with continental trajectories (Figure 5). However, these differences are not significant. Neither are significant the geometric mean differences of 4,4'-DDE showing similar levels in the samples with continental and oceanic trajectories, 4.4 and 3.1 pg m^{-3}, respectively. Thus, the concentration changes of PCBs and 4,4'-DDE are not so clearly defined as in the case of Sklanante Pleso.

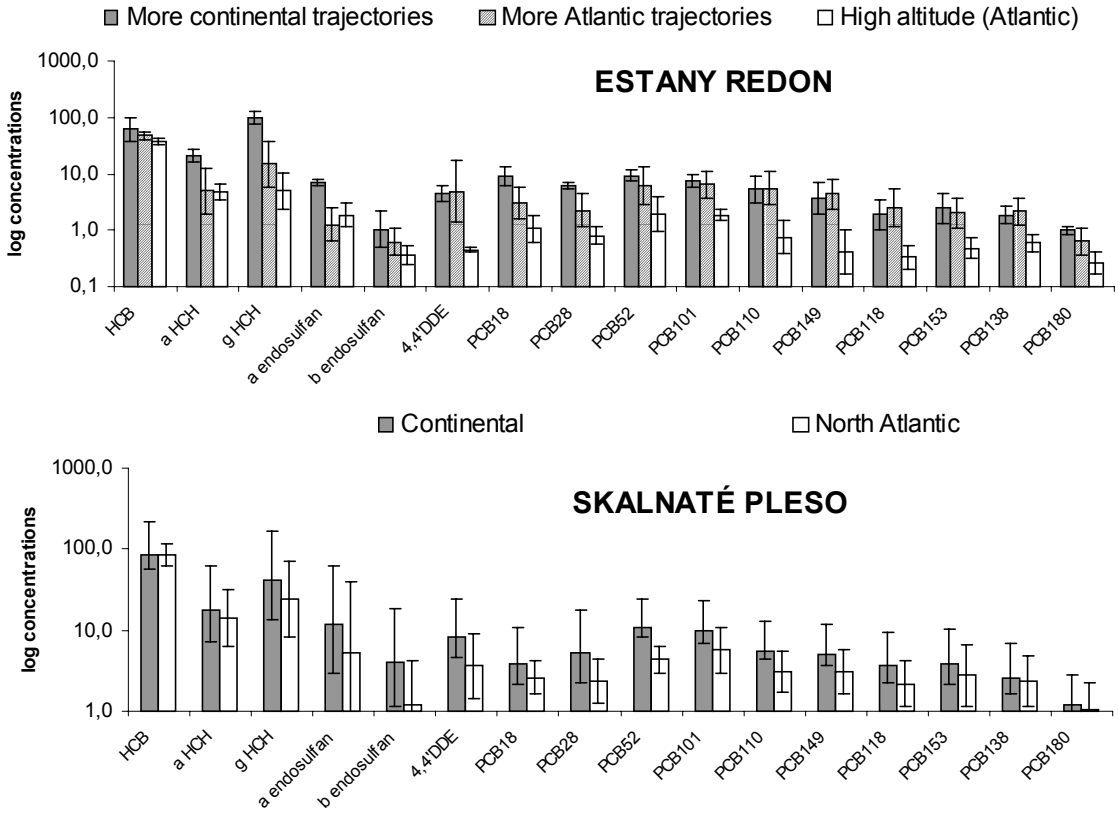

Figure 5. Geometric means of the composition of major (gas phase) organochlorine compounds in the air masses collected at Estany Redon corresponding to predominant continental, oceanic and high altitude origin. Similarly for Skalnate Pleso for continental and oceanic origin. Error bars indicate standard deviation.

In contrast, strong differences are found among the compounds of present use, HCHs and endosulfans. Thus, their gas phase geometric means are 250 and 17 pg m^{-3} in the continental air masses and 13 and 1.9 pg m^{-3} in the more oceanic air masses. The ratios of $\alpha/(\alpha+\gamma)$ HCH in Estany Redon are 0.19±0.06 and 0.27±0.07 for the air masses of continental and Atlantic origin, respectively, whereas those of Skalnaté Pleso are 0.30±0.06 and 0.37±0.09, respectively. In both cases, the trajectories of more marine origin are enriched in the α-isomer which is consistent with the high proportion of α-HCH with respect to the other isomers in oceanic waters (29, 37).

A strong difference in SOC concentration is found for the high altitude group which exhibits significantly lower geometric mean concentrations for HCH, endosulfans, 4,4'-DDE and PCB, 9.8, 2.2, 0.4 and 9.0 pg m^{-3}, respectively. Air masses that travel at low altitudes can incorporate SOCs easier than air masses that travel at high altitude, since the first are closer to potential pollution sources and the later are more exposed to weathering processes. The proportion of α-HCH isomer in the samples corresponding to air masses at very high altitude is even higher than the previous values, 0.49±0.11, which is again in agreement with the high α-HCH content found in aircraft measurements at high altitude (21).

These three groups defined from air mass origin, more continental, more oceanic and high altitude, correspond to different in situ air sampling temperatures 9ºC, 4.3ºC and 0.3ºC, respectively. The coincidence between higher air mass trajectories and lower in situ temperatures reflects that the winter atmosphere is in general more stable than the summer atmosphere (38). Again, the correspondence observed between air sampling temperatures at this site and SOC concentrations can be related to LRAT. Evaluation of the origin of the air masses illustrate that the origin of these SOC is mainly related to surface sources located in Europe.

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Article 5.

PCBS IN PINUS UNCINATA, THE UPPERMOST GROWING TREE SPECIES OF CENTRAL PYRENEAN HIGH MOUNTAINS (CATALONIA, SPAIN)

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PCBs in *Pinus uncinata*, the uppermost growing tree species of Central Pyrenean high mountains (Catalonia, Spain)

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Key words: Polychlorobiphenyls, remote environments, long-range transport of pollutants, organochlorine compounds in biota, higher plants

Abstract

The polychlorobiphenyl (PCB) composition of pine needles of *Pinus uncinata* from Pyrenean high mountains has been investigated. Samples from four altitudes (1750 m, 1950 m, 2150 m and 2250 m) were collected in March 2002 and June 2002 in a central area near the Lake Redon. Average atmospheric temperatures at these sampling sites were also determined. The observed concentrations were similar to those found in pine trees from rural areas in Europe. Highest PCB levels were generally found at higher altitude, e.g. the most remote sites. A correlation between log-transformed PCB concentrations and reciprocal of absolute average air temperature was observed for the less volatile congeners. Highest concentrations were found at lowest temperatures. Phase change enthalpies calculated from the slopes of the concentration-temperature dependences showed a good agreement with the enthalpies of vaporization.

The pine needle-atmosphere partition coefficients of the studied PCB congeners increased with higher degree of compound chlorination and with lower average air temperatures. They exhibit a good linear relationship with $\log(K_{oa})$ but the temperature dependence is stronger for $\log(K_{pa})$ than $\log(K_{oa})$.

Estimation of the PCB atmospheric concentrations at different mountain levels using $\mathrm{Log}(K_{pa})$ and pine needle concentration data predicted lower values at higher altitude (lower air temperatures), in the order of 2.1 and 1.3 times, consistently with analytical measurements at similar levels performed in previous studies.

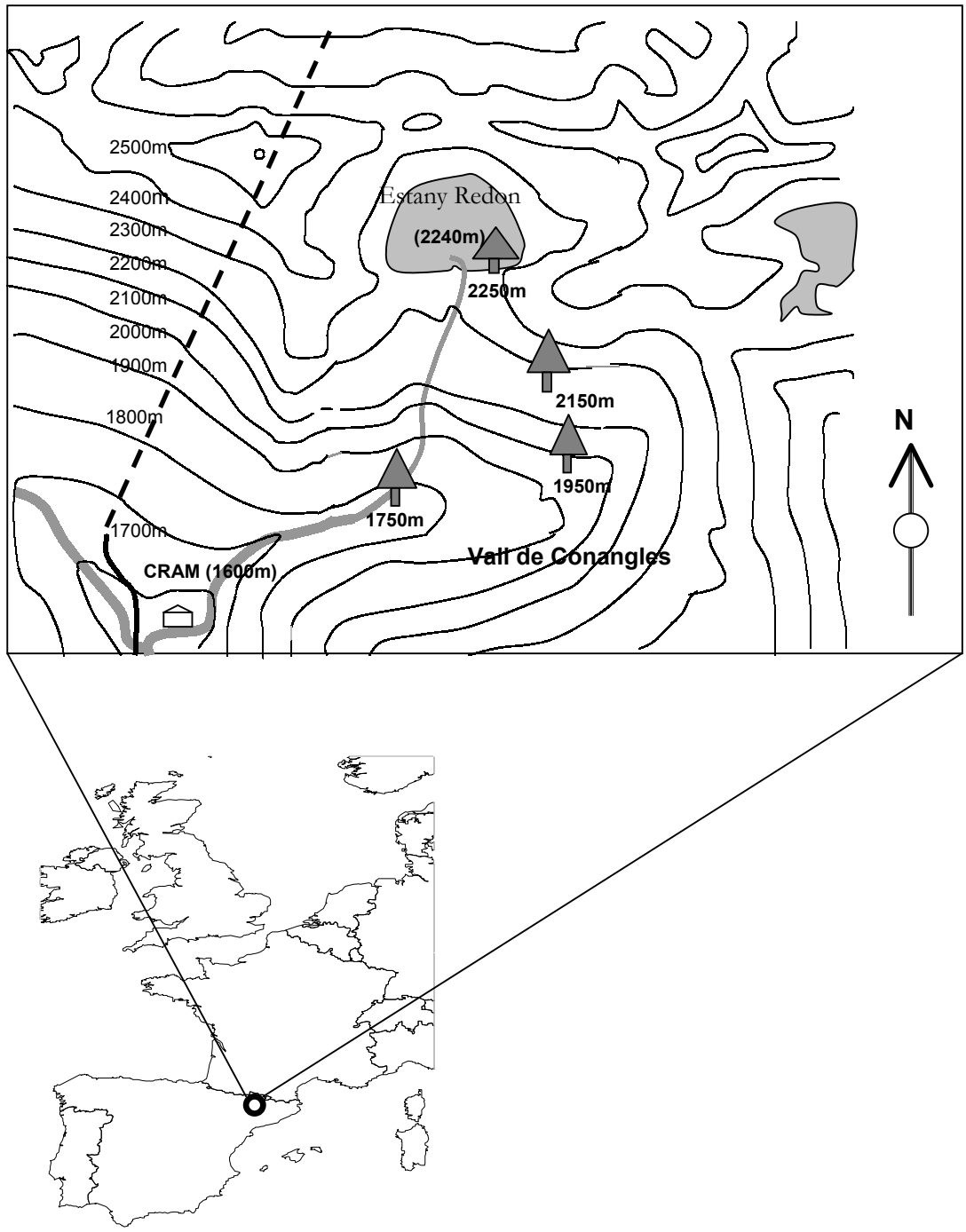

Figure 1. Sampling sites of *Pinus uncinata* needles in the Vall de Conangles and Lake Redon.

1. Introduction

In the recent years, semi-volatile organic compounds, like polychlorobiphenyls (PCBs), have been detected in the atmosphere and other environmental matrices of remote areas, including high-mountains (Calamari et al., 1991, Carrera et al., 2002, Vilanova et al., 2001, Grimalt et al., 2001, van Drooge et al., 2002). These areas are characterized by the absence of local contamination sources being impacted by long-range atmospheric transport of pollutants.

PCB have high octanol/water partitioning coefficients ($\log K_{ow} > 4$) and show affinity for organic materials such as pine tree needles (Gaggi and Bacci, 1985; Schonherr and Reiderer, 1989, Umlauf et al., 1994). In this respect, the pine species, *Pinus uncinata*, constitutes the dominant tree species at the timberline of the Central Pyrenees. This species can therefore be useful as sentinel organism for atmospheric pollution in these remote alpine-subalpine zones.

In present study, the potential of *Pinus uncinata* to monitor long-range transported pollution to high mountains such as the Central Pyrenees is investigated. This species has been measured in an altitude gradient between 1750 m and 2250 m (Figure 1). Samples in this gradient were collected in March and June 2002. The observed concentrations have been evaluated in terms of altitude and average air temperature dependence. They have also been compared with atmospheric PCB data measured at Lake Redon (42º38'34"N, 0º46'13"E, 2250 m) simultaneously to leave sampling. Phase change enthalpies between atmosphere and leave surfaces have therefore been calculated. The results have also been used to predict atmospheric PCB levels at other altitudes.

2. Materials and Methods

2.1. Materials

Residue analysis-grade *n*-hexane, dichloromethane, iso-octane, methanol and acetone were from Merck. Anhydrous sodium sulphate for analysis was also from Merck. Neutral aluminum oxide type 507C was from Fluka AG and silica gel was from Panreac. Cellulose extraction cartridges were from Whatman Ltd. Aluminum foil was rinsed with acetone and let dry at ambient temperature prior to use. The purity of the solvents was checked by gas chromatography-electron capture detection (GC-ECD). We detected no significant peaks for any of the reagents. Aluminum oxide, silica gel, sodium sulphate and cellulose cartridges were cleaned by Soxhlet extraction with hexane:dichloromethane (4:1, v/v) during 24 h before use. The purity of the cleaned reagents was checked by ultrasonic extraction with *n*-hexane:dichloromethane (4:1; 3 x 20 mL), concentration to 50 μL and analysis by GC-ECD. No interferences were detected. Aluminum oxide, silica gel and sodium sulphate were activated overnight at 400ºC, 120ºC and 110ºC, respectively. Aluminium oxide and silica gel were deactivated with 5% Milli-Q water.

2.2. Sample collection

Samples were collected with pre-cleaned tweezers, stored in glass tubes and transported to Barcelona at < 0ºC. There, they where stored at –20ºC until analysis.

2.3. Extraction and clean up

Whole pine needles (1-4 g fresh weight) of each sample were Soxhlet extracted for 24 h in 100 ml dichloromethane inside a pre-cleaned glassfiber cartridge containing 5 g Na_2SO_4. Internal standards of PCB#30 and PCB#209 were added to all samples and blanks before extraction. Then, the extract was evaporated until 0.5 ml by vacuum rotary evaporation and clean up with a two-layer column (diameter 1 cm) filled with slurry packing in hexane with 8 g of silica gel (bottom) and with 8 g neutral aluminium oxide (top). The column was topped with 0.5 g of Na_2SO_4. The column was then eluted with 20 ml of hexane and additionally with 20 ml hexane/dichloromethane (19:1 v/v) for PCB elution. The recovered fractions were vacuum evaporated to 0.5 ml, transferred to vials and then further concentrated under a gentle N_2-gas stream and redissolved in 50µl of isooctane.

2.4. Dry weight and lipid content

Dry weight (DW) and hexane-extractable lipids (HEL) were determined from sample aliquots (0.5-2 g). These aliquots were dried at 100ºC for 24 hours in a hot air oven for DW. For HEL the dried needles were extracted two times with 20 ml of hexane in an ultrasonic bath for 15 minutes. The combined extracts were then vacuum evaporated to 0.5 ml and transferred to a pre-weighted vial where they were concentrated further under a gentle stream of N_2 until constant weight. HEL were calculated gravimetrically.

2.5. Instrumental analysis

Samples were injected in a TraceGC 2000 (Finnigan) series chromatograph coupled to a MS Agilent 5973 series. An HP-5 fused silica capillary column (30 m length, 0.25 mm i.d, 0.25 μm film thickness) coated with 5% phenyl 95% methylpolysiloxane was used for the analyses. The oven temperature program started at 100°C (holding time 1 min), increased to 120°C at 20°C·min^{-1}, to 240ºC at 4°C·min^{-1} (holding time 12 min) and finally to 300°C at 4°C·min^{-1} (holding time 10 minutes). Injector, ion source, quadrupole and transfer line temperatures were 280°C, 200ºC, 150ºC and 310°C, respectively. Helium was used as carrier gas (0.9 ml s^{-1}). The MS was operating in selective ion monitoring (SIM) with electron impact (71 eV). Dwell time was 50 ms channel^{-1}. Quantification was performed by external standard method and corrected for surrogate recoveries. The PCB congeners analyzed in this study encompassed #28 (m/z=256, 186), #52 (m/z=292, 220), #101 (m/z=326, 254), #153 (m/z=360, 290), #138 (m/z=360, 290) and #180 (m/z=394, 324).

2.6. Atmospheric PCB concentrations

The atmospheric concentrations used in this study for calculation of the distribution coefficients were obtained from samples collected at Lake Redon (2240 m) simultaneously to pine needle collection. The sampling method, analytical procedure and results are described elsewhere (van Drooge et al., submitted).

Table 1. Concentrations of PCB congeners (ng g^{-1} dry weight) in pine needles of *Pinus uncinata* from the Pyrenean high mountains.

March 2002									
Sample nº	altitude (m)	DW (%)	PCB 28	PCB52	PCB 101	PCB 153	PCB 138	PCB 180	∑PCB
1	2250	49	0.21	0.66	1.2	0.77	0.86	0.59	4.3
2	2150	49	0.25	0.80	1.2	0.85	1.0	0.69	4.8
3	1950	48	0.25	0.72	1.2	0.74	0.87	0.60	4.4
4	1750	49	0.20	0.64	1.1	0.65	0.77	0.52	3.9
June 2002									
Sample nº	altitude (m)	DW (%)	PCB 28	PCB52	PCB 101	PCB 153	PCB 138	PCB 180	∑PCB
1	2250	53	0.18	0.58	0.84	0.54	0.64	0.31	3.1
2	2150	60	0.23	0.57	0.89	0.56	0.65	0.37	3.3
3	1950	51	0.20	0.55	0.86	0.59	0.64	0.41	3.3
4	1750	52	0.22	0.57	0.79	0.50	0.60	0.29	3.0

3. Results and Discussion

3.1 Site of study

Needles from *Pinus uncinata* were collected in the Vall de Conangles and near the high mountain Lake Redon in the central Pyrenees at heights of 1750 m, 1950 m, 2150 m and 2250 m (Figure 1). The sites selected for study encompass sub-alpine to alpine environments. In this region, *Pinus uncinata* grows between 1700 m and 2400 m and is the last growing tree species at the local tree-line. Above 2000 m the appearance of this species becomes sparse and the size of the individuals is smaller. The highest site has an average annual ambient temperature of 3.7ºC (data from 2002) and a snow cover between November and May. The lowest site has an average annual ambient temperature of 8.3ºC (data from 2002). Samples were collected at heights of 1750 m, 1950 m, 2150 m and 2250 m in March and June 2002. Each sample is a composite of leaves older than one year from four different trees. Pine needles older than one year are assumed to have PCB concentrations not influenced by growth changes.

3.2. Temperature data

Average air temperatures (T_a) were obtained from the registers of the meteorological stations situated at Lake Redon (2240 m) and at the Centre of High Mountain Research (CRAM) (1600 m). Both stations are located in the same valley and near the sample sites.

At Lake Redon, T_a were calculated from measurements taken every 30 min. They provided values of 1.4ºC and 15.9ºC for March and June 2002, respectively. At CRAM, T_a were calculated

from the minimum and maximum daily temperatures which resulted into average values of 10.0ºC and 19.0ºC, respectively.

These T_a were used to calculate altitude lapse rates for the sampling sites at 1750 m, 1950 m and 2150 m. In March and June 2002 these rates were 1.3ºC/100 m and 0.5ºC/100 m, respectively. Thus, T_a for 1750 m, 1950 m and 2150 m were 8.0ºC, 5.4ºC and 2.7ºC in March 2002, respectively, and 18.3ºC, 17.3ºC and 16.4ºC in June 2002, respectively.

3.3. PCB concentrations in Pinus uncinata

The concentrations of individual PCB congeners ranged between 0.2 $ng \cdot g^{-1}$ DW and 1.2 $ng \cdot g^{-1}$ DW in March. In June the concentrations ranged between 0.2 $ng \cdot g^{-1}$ and 0.9 $ng \cdot g^{-1}$ (Table 1). These concentrations are similar to those found in pine needles from urban/rural areas (Jensen et al., 1992, Müller et al., 2001), and slightly higher than those from remote areas of Scandinavia (Brorström-Lundén and Löfgren, 1998).

The composition of PCBs is similar in both sample periods (Figure 2). PCB#101 predominated in all cases (27%), followed by #138 (20%), #153 (17%), #52 (17%), #180 (12%) and #28 (6%). This composition is similar to the one found in spruce needles of the Swedish west coast (Brorström-Lundén and Löfgren, 1998). At all sample sites the PCB levels are about 1.3 times higher in March than in June (Figure 2). Only the more volatile PCB#28 does not show significant differences ($p>0.05$).

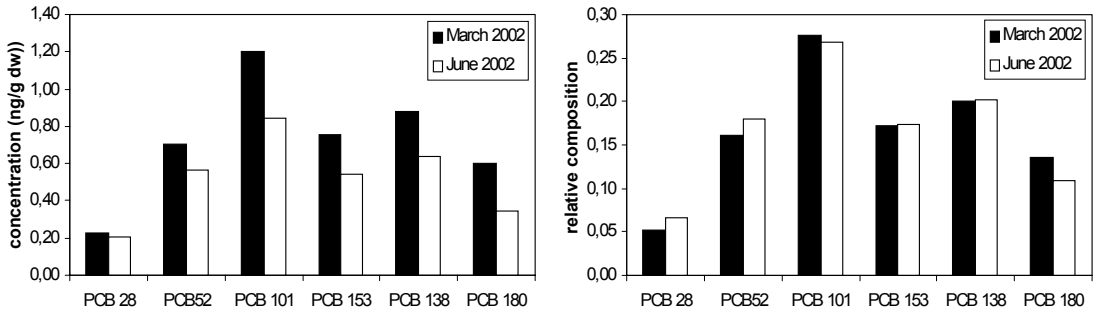

Figure 2. Average concentrations (top) and relative composition (bottom) of PCB in the *Pinus uncinata* needles collected in March and June 2002.

3.4. Concentration dependence with altitude and temperature

Representation of the March and June pine needle log-transformed concentrations vs. altitude shows a significant gradient in some PCB congeners, e.g. #101, 153, 138 and 180 in March and #138 in June (Table 2). This altitude gradient involves higher concentrations at the higher sites. Thus, the most remote sites (highest altitude) are those most polluted.

Table 2. Correlation coefficients (r^2) of the PCB concentrations in pine needle and altitude (data collected in March and June separately) and average air temperatures (all data).

$\log(K_{pa})$	Altitude (March samples)	Altitude (June samples)	Temperature (All)
PCB 28	0.056	0.196	0.157
PCB 52	0.162	0.196	0.798
PCB 101	0.477	0.523	0.938
PCB 153	0.689	0.145	0.897
PCB 138	0.452	0.767	0.916
PCB 180	0.482	0.049	0.856

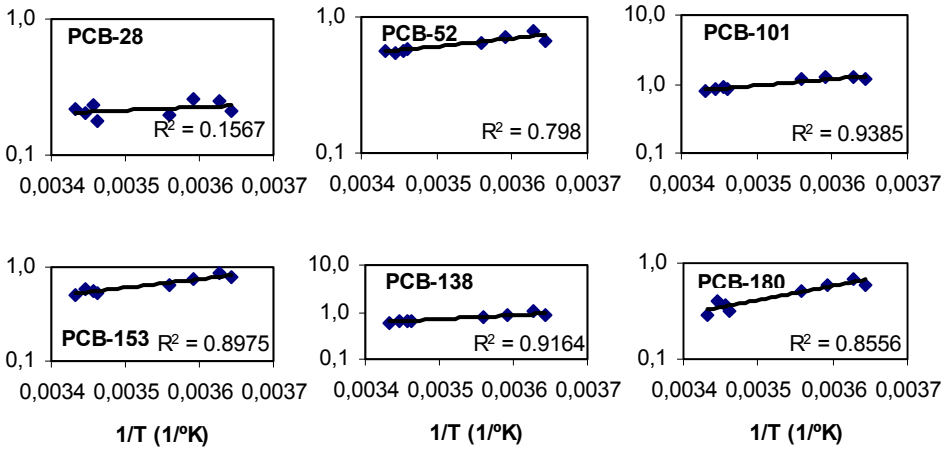

Figure 3. Correlation of the PCB composition in *Pinus uncinata* needles and average air temperatures

However, the underlying factor for the altitude gradient is temperature. Thus, joint representation of the log-transformed PCB concentrations in the samples collected in March and June vs. reciprocal of temperature (in K) shows very high correlation coefficients (r^2 between 0.798 and 0.938) for all PCB congeners except #28 (Table 2). These high correlation coefficients correspond to well defined linear fittings between log-transformed concentrations and 1/T (Figure 3), lower temperatures involving higher concentrations. This trend in consistent with previous observations on concentration of organochlorine compounds in fish muscle and sedimentary inventories obtained from a series of high mountain lakes distributed over Europe (Grimalt et al., 2001). In this study, a strong correlation of the concentrations of PCB congeners #101, 153, 138 and 180 with temperature and altitude was also observed. Again, lower temperatures involved higher PCB concentrations. Thus, the pine needle results provide new data supporting the selective accumulation of some PCB in high mountain areas which, in turn, is consistent with the predictions of the global distillation theory (Wania and Mackay, 1993).

The lack of correlation of PCB#28 with temperature in pine needles is also consistent with the previous data. Thus, in the fish and sediment study the temperature dependence was only observed for the less volatile PCB congeners, not for PCB #28 and #52 (Grimalt et al., 2001). In

the present case, the most volatile congener examined, PCB #28 does not show temperature correlation and PCB#52 exhibits a significant correlation coefficient but the lowest among those of the temperature dependent congeners. When the pine needle concentrations are normalized to lipid content the temperature dependence is only maintained for some PCB congeners, e.g. #180.

Contaminants in the gas phase diffuse into the interior of the needles via the stomata, the wax and the cuticle wall, so it may be that the whole pine needle provides an improved matrix for atmospheric contaminants over the surface wax only (Reischl et al., 1987, Jensen et al., 1992, Umlauf et al., 1994).

3.5. Pine needle/air partition distribution coefficients (K_{pa})

Air concentrations were measured at 2250 m (Lake Redon) in March and June during leave sampling. The obtained values can be used to calculate pine needle/air partition coefficients at this site during these two periods (cold and warm, respectively). Obviously, the calculation assumes that the exchange of PCBs between the atmosphere and pine needles has reached steady state conditions. Steady state is expected in view of the good temperature dependences described in the previous section.

The partitioning of PCB between atmosphere and tree leaves can be described by a pine needle/air-partitioning coefficient (K_{pa}) defined as:

$$K_{pa} = C_p/C_a \quad (1)$$

where C_p is the pine needle concentration (pg kg^{-1} dry weight) and C_a is the atmospheric concentration (pg L^{-1}).

Table 3. Pine needle/air partition coefficients log(K_{pa}) and phase change enthalpies for PCBs in *Pinus uncinata* at 2250m.

logK_{pa}	March	June	Slope (x10^3)	ΔH_{pa}	ΔH_{vap}*
PCB 28	8.4	7.7	3.92	75	78
PCB52	8.5	8.0	2.84	54	81
PCB 101	8.8	8.1	3.99	76	85
PCB 153	9.2	8.2	5.16	99	91
PCB 138	9.1	8.3	4.47	86	92
PCB 180	9.3	8.4	5.29	101	97

* Obtained from Kömp and McLachlan, 1997a.

Log(K_{pa}) in March and June increase at higher degree of PCB chlorination (Table 3). They are also higher at lower ambient temperature. That is, the March samples (Table 3). In general it is assumed that gas-solid surface coefficients such as log(K_{pa}) are proportional to the octanol/air partition coefficients log(K_{oa}) (Paterson et al., 1991; Bacci et al., 1990; Gobas et al., 1991). This relationship is effectively observed when comparing the pine needle and the atmospheric

concentrations of both March and June samples from the present study (Figure 4). The $\log(K_{oa})$ values were obtained from the equation

$$K_{oa} = K_{ow}\, RT / H \qquad (2)$$

where K_{ow} is the octanol/water partition coefficient (Mackay et al., 1992), R is the gas constant (8.314 $J \cdot {}^{o}K^{-1} \cdot mol^{-1}$), T is ambient temperature and H is the Henry constant (Dunnivant et al., 1992). H was corrected for ambient temperature using the phase change enthalpies of octanol/water from Kömp and McLachlan (1997a).

The regression lines for March (1.4ºC) and June (15.9ºC) are significantly different ($p<0.001$). The March plot shows both higher $\log(K_{pa})$ and $\log(K_{oa})$ values. The slopes of the regression lines are 0.56 and 0.37 for March and June, respectively. The increase of the slope at lower temperature shows that K_{pa} has stronger temperature dependence than K_{oa}. This difference has also been observed in previous studies with other plant species (Kömp and McLachlan, 1997b). In the case of *Pinus uncinata* the low slopes shown in Figure 4 indicate that K_{pa} and K_{oa} do not behave similarly upon temperature change.

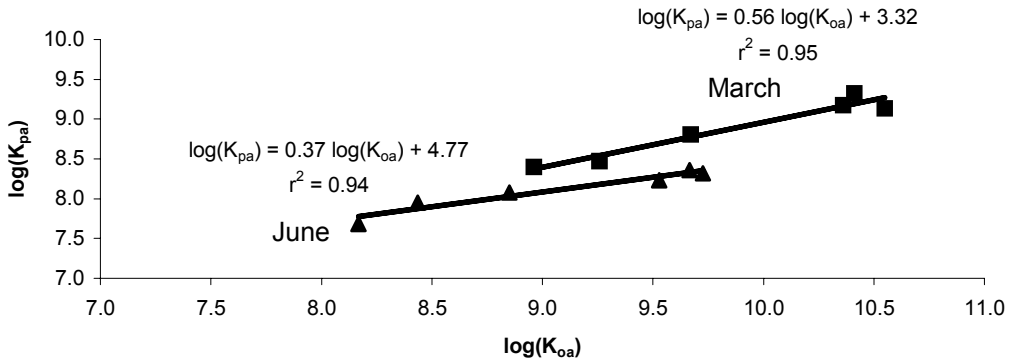

Figure 4. $\text{Log}(K_{pa})$ vs $\log(K_{oa})$ of the concentrations of PCB congeners #28, #52, #101, #153, #138 and #180 in *Pinus uncinata* collected in March and June.

3.6. Temperature dependence of K_{pa}

Representation of K_{pa} vs. T_a provides slopes in the 2.84-5.29 range (Table 3). These values are similar to those found in other species (Kömp and McLachlan, 1997b) and increase with higher chlorination of the PCBs (Table 3). The slopes can be used to calculate phase change enthalpies from pine needle to air using the following expression

$$\Delta H_{pa} = 2.303\, RS \qquad (3)$$

where S is the slope, 2.303 is the factor of correction for common to natural logarithm (ln(10)) and R is the gas constant (8.314 $J \cdot {}^{o}K^{-1} \cdot mol^{-1}$).

The calculated ΔH_{pa} range between 54 and 101 $kJ \cdot mol^{-1}$ (Table 3). As expected from the above discussed slope values, the atmosphere-pine needle phase change enthalpies increase at increasing degree of chlorination of the PCB congeners. Comparison of these values with the theoretical enthalpies for vaporization of the subcooled liquid, ΔH_{vap}, shows a very good agreement indicating that transfer between these two environmental compartments is driven by vaporization/condensation processes.

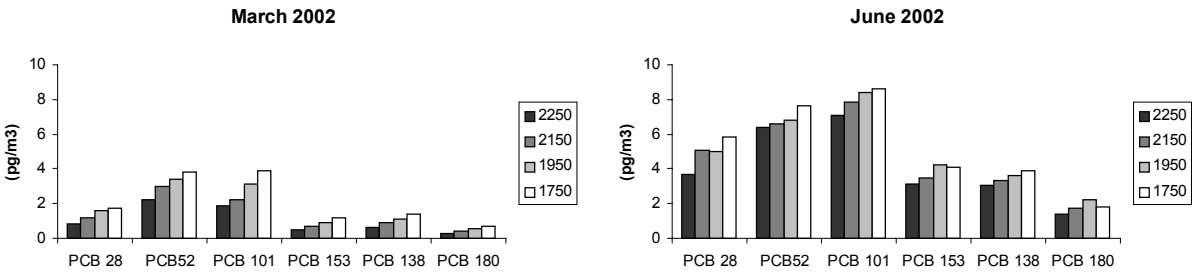

Figure 5. Estimated atmospheric PCB levels at different altitudes based on the K_{pa} coefficients and the pine needle concentrations.

3.7. Estimation of atmospheric concentrations from Pinus uncinata data

The observed dependence between K_{pa} and temperature (Table 3) allows the estimation of K_{pa} at different altitudes. Then, the estimated constants can be used to predict atmospheric concentrations if the pine needle concentrations at these altitudes are known (equation 1). The results of this approach for the altitude gradients considered in the present study are shown in Figure 5. Decreasing atmospheric PCB levels at increasing altitude is predicted. Between 2250 m and 1750 m these decreases involve ratios of 2.1±0.3 times and 1.3±0.1 times in March and June, respectively. Again, the underlying reason of change is temperature, the differences being higher at lower values. These decreases are consistent with values of 1.8 times obtained from measurements of the differences in atmospheric PCB concentrations between Redon Lake (2250 m) and CRAM (1600 m) in January 2003 using a HiVol-sampler.

4. Conclusions

The PCB concentrations in the pine needles of *Pinus uncinata* from Central Pyrenean high mountains are similar to those found in pine trees from rural areas in Europe. Highest PCB levels were generally found at higher altitude, e.g. the most remote sites, as consequence of the lower temperatures at higher altitudes. A strong correlation between log-transformed PCB concentrations and reciprocal of absolute average air temperature has therefore been observed. Highest

concentrations were found at lowest temperatures. The correlation is observed for all PCB congeners considered in the study except #28 which is in agreement with previous data on fish concentrations and sediment inventories showing that the less volatile PCB congeners accumulate selectively with temperature dependence. Phase change enthalpies calculated from the slopes of the concentration-temperature dependences show a good agreement with the enthalpies of vaporization. Overall, the concentrations exhibit good steady state conditions being in equilibrium with the environmental. This pine species is therefore useful as sentinel organism for monitoring the levels of atmospheric PCB pollution in high mountain areas.

Log(K_{pa}) range between 8.4-9.3 and 7.7–8.4 in March and June, respectively. These partition coefficients increase with higher degree of congener chlorination and with lower average air temperatures. They exhibit a good linear relationship with log(K_{oa}) but the slopes of the correlations are lower than one, 0.37-0.56, indicating stronger temperature dependence of Log(K_{pa}) than log(K_{oa}). Estimation of the PCB atmospheric concentrations at different mountain levels using Log(K_{pa}) and pine needle concentration data predicts lower values at higher altitude (lower air temperatures), in the order of 2.1 and 1.3 times, which is consistent with analytical measurements at levels of 1600 m and 2240 m (1.8 times).

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Article 6.

PASSIVE SAMPLING OF ATMOSPHERIC ORGANOCHLORINE COMPOUNDS BY SPMDS IN A HIGH-MOUNTAIN AREA (CENTRAL PYRENEES)

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Passive sampling of atmospheric organochlorine compounds by SPMDs in a remote high-mountain area

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Abstract

Since the ban of most the organochlorine compounds their atmospheric concentrations in remote areas have only decrease little, if any, and therefor it is of interest to study the evolution of the atmospheric SOC levels on a long time range. Passive air samplers, such as Semipermeable Membrane Devices (SPMDs) allow time-integrated sampling of the atmosphere without the need f energy supply, which makes them ideal for deployment in remote areas over long periods. Triolein containing SPMDs were exposed for 1.5 years to the atmosphere in the Central Pyrenees (Catalonia, Spain), and were analyzed for HCB and PCBs. The performance reference compound (PRC) method was applied to calibrate the sampling rates of the SPMDs in situ. The purpose of the present study was to assess atmospheric concentrations of HCB and PCBs along a height gradient (1600-2600 m) and to validate sampling by SPMDs against sampling by HiVols. Sampling rates between 0.55 and 1.3 m^3 d^{-1} were observed for the performance reference compound PCB155. Although errors in the application of physico-chemical properties in the model calculations may cause considerable uncertainties in the obtained sampling rates, the observed atmospheric concentrations obtained by the SPMD were in good agreement with the observed atmospheric concentrations obtained by HiVols. These findings suggest that SPMDs can be applied as monitoring systems of the atmospheric concentrations of organochlorine compounds in these remote high mountain areas.

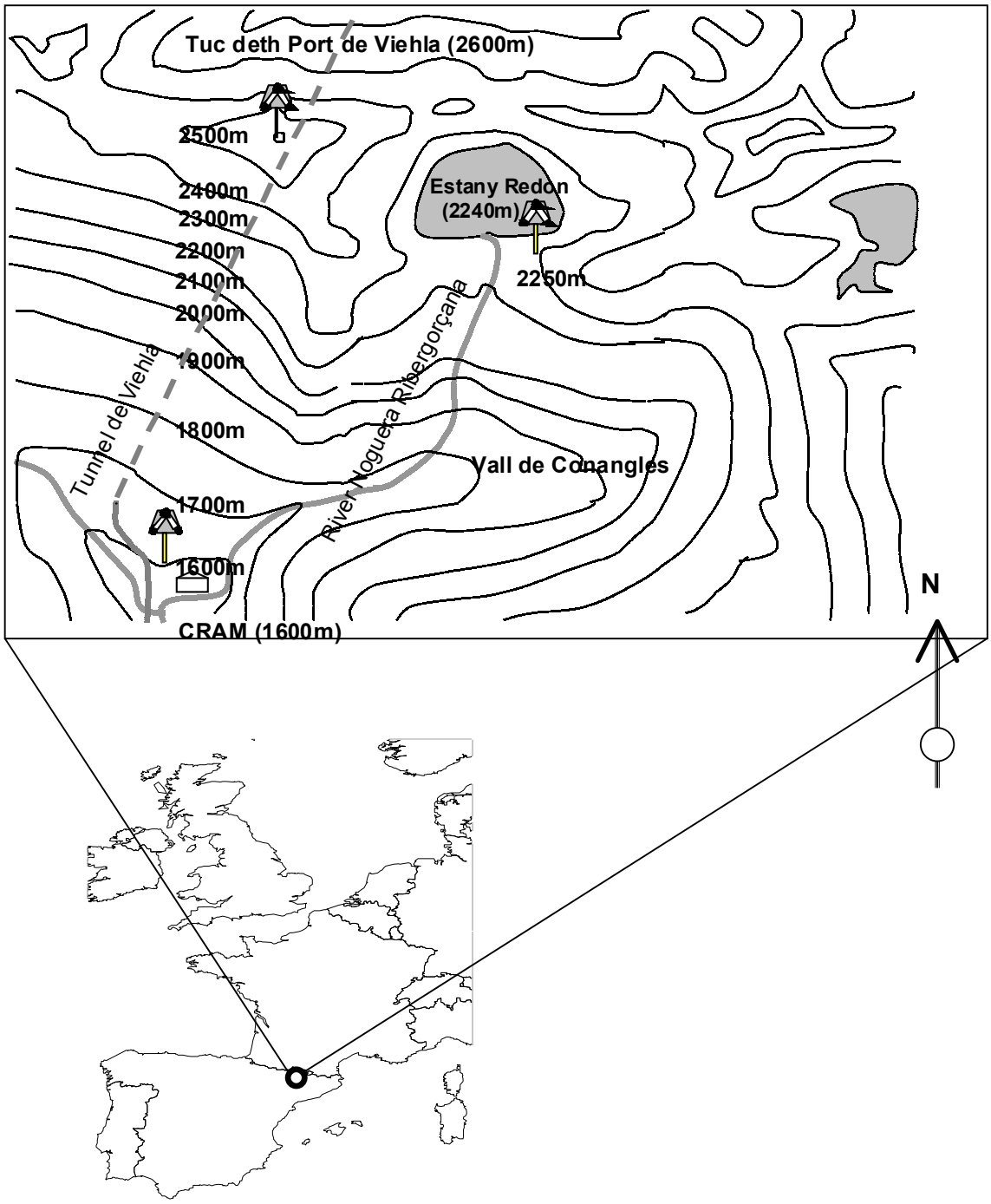

Figure 1. Location of the SPMD sampling sites near Estany Redon (central Pyrenees, Catalonia, Spain)

Introduction

In recent years semi-volatile organic compounds, such as hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB), have been detected in remote high-mountain sites (1-4). Due to their relatively high vapor pressure (10^{-1} – 10^{-4} Pa) and resistance against degradation during atmospheric transport, these compounds are widely spread into high mountain areas, where they were never produced or used (3, 5). Although, their production and use are prohibited or restricted now for many years, there has only been a clear decline in concentrations in areas of production and application (6). At remote sites the decrease of atmospheric concentrations is little, if any, and HCB and PCBs are still detected at trace levels (7). This is of concern since these compounds may cause toxic effects (8-9). It is therefore of interest to study the evolution of the atmospheric SOC levels at remote sites, like mountain areas, on a long time range.

Atmospheric contaminant levels are typically assessed using conventional high-volume (HiVol) samplers. These samplers suffer from a number of methodological difficulties, such as adsorption of gaseous analytes to the glass fibre filter, desorption of particle-bound compounds, and the snap-shot image these devices produce of the possibly highly variable atmospheric concentrations (10). In addition, the operation of HiVol samplers in remote areas requires the use of generators, adding to logistical difficulties.

Semi-permeable membrane devices (SPMDs) have been used since 1993 for sampling of atmospheric organic contaminants, both in remote and in densely populated areas (10-15). These samplers allow for time-integrative sampling of the contaminants, and do not require a power supply, which makes them ideal for deployments in remote areas.

Standard-design SPMDs consist of a low-density polyethylene lay-flat tubing (wall thickness of 75-95 μm) filled with 20% (w/w) triolein (1,2,3-tri[cis-9-octadecenoyl]glycerol), with a surface area of about 460 cm^2 per mL triolein (16). Concentrations in air (C_a) can be calculated from the absorbed amounts (N_s) by (14, 15, 17).

$$N_s = C_a K_{sa} V_s [1-\exp(-k_e t)] \quad (1)$$

where K_{sa} is the SPMD-air partition coefficient, V_s is the SPMD volume, and t is the exposure time. The (first order) exchange rate coefficient (k_e) is defined by (17-18)

$$k_e = k_o A / K_{sa} V_s \quad (2)$$

where A is the SPMD surface are, and k_o is the overall mass transfer coefficient. For short exposure times (kinetic sampling), equation 1 reduces to

$$N_s = C_a k_o A t \quad (3)$$

$$= C_a R_s t \quad (4)$$

From analyses of SPMD with different exposure times Ockenden et al. (13) observed a linear uptake of PCBs. The air sampling rates (R_s) were calculated by dividing the atmospheric concentrations (C_a) obtained with HiVols by the uptake rates. A drawback of this method is that the R_s can only be calculated if atmospheric concentrations are available, or if it is assumed that R_s will not differ among locations. Moreover, this calculation is only possible at short exposure times, when the uptake is linear. If equilibrium sampling has been reached, after long exposure time, an underestimation of atmospheric concentrations will be a result of this method.
Combining equations 2 - 4, the air sampling rate (R_s) can be written as

$$R_s = k_o A = k_e K_{sa} V_s \quad (5)$$

For long exposure times (equilibrium sampling), equation 1 reduces to

$$N_s = C_a K_{sa} V_s \quad (6)$$

which shows that C_a can be calculated using the SPMD-air partition coefficient. The advantage of using equation 1 is that it covers both the kinetic sampling and the equilibrium sampling phase, as well as the intermediate phase (19) Good estimates of k_e and K_{sa} should be available, however. To our knowledge, no published K_{sa} values exist, but reasonable estimates can be obtained from SPMD-water partition coefficients (K_{sw}) and Henry's law constants (H)

$$K_{sa} = K_{sw} R T / H \quad (7)$$

where R is the gas law constant , and T is the absolute temperature. The group H/RT represents the air-water partition coefficient in volume concentration units. SPMD-water partition coefficients of HCB and PCBs have been shown to be independent of temperature (18, 20). A strong temperature dependence can be expected for K_{sa}, because Henry's law constants increase strongly with increasing temperature (21, 22). Exchange rate constants can be obtained from the dissipation of performance reference compounds (PRCs) that are spiked into the SPMDs prior to exposure (20). When PRCs are chosen that do not occur in significant levels in the environment, such as PCB29 and PCB155, the k_e values for these compounds can be obtained from

$$k_e = - \ln (N / N_0) / t \quad (8)$$

where N is the PRC amount remaining after the deployment, and N_0 is the amount that was initially present in the SPMD at $t = 0$ (20). Typically, only PRCs with a narrow volatility range can be used to calculate k_e. Compounds with smaller K_{sa} values will have dissipated to below their detection limit, and PRCs with higher K_{sa} values will often show a decrease that is too small to quantify. When the exchange kinetics between air and SPMDs are controlled by the air boundary layer, some basic models can be applied to calculate k_e values for all compounds, using the measured k_e of a

single PRC. For boundary layer controlled uptake the overall mass transfer coefficient is equal to the mass transfer coefficient for the boundary layer ($k_o \approx k_a$)

$$k_e = k_a A / K_{sa} V_s \quad (9)$$

Therefore, PRC-based exchange rate coefficients ($k_{e,PRC}$) can be used to calculate the coefficients for other compounds (k_e) using

$$k_e = k_{e,PRC} (K_{sa,PRC} / K_{sa}) (k_a / k_{a,PRC}) \quad (10)$$

Mass transfer coefficients for fluid boundary layers are typically proportional to the 2/3 power of the molecular diffusion coefficient (23-25). Hence,

$$k_e = k_{e,PRC} (K_{sa,PRC} / K_{sa}) (D_a / D_{a,PRC})^{2/3} \quad (11)$$

The dominant factor in equation 11 is the ratio of SPMD-air partitioning coefficients, which differ between compound by order of magnitudes. The ratio of diffusion coefficients is typically quite small. For example, the ratio of diffusion coefficients of HCB and PCB180 as calculated from the Fuller, Schettler & Gillings equation (26) is only a factor of 1.2.

Little is known about whether the uptake from air is indeed controlled by the boundary layer or instead by the membrane. For water-SPMD exchange, membrane controlled uptake results in a log R_s versus log K_{ow} slope that is close to (but somewhat smaller than) unity, whereas boundary-layer controlled uptake results in log R_s - log K_{ow} slopes that are slightly negative (18). For uptake by SPMDs from air, a similar reasoning may be applied. Ockenden et al. (13) report that sampling rates for tri- to heptachloro biphenyls increase with log K_{oa}. For tri- and tetrachlorobiphenyls (log K_{oa} <8.2), the log R_s versus log K_{oa} slope ranges between 0.4 (winter data) and 0.7 (summer data), indicating predominantly membrane controlled uptake. For penta- to heptachlorobiphenyls (log K_{oa} >8.8) the log R_s - log K_{oa} slopes are 0.0 (summer) and 0.1 (winter), which is indicative of boundary-layer controlled uptake. Lohman et al. (10) report that the sampling rates of PAHs with 5 to 6 aromatic rings (log $K_{oa} \approx 11$) decrease with molecular size, and that the ratio of sampling rates of tetra- and pentachloro dibenzo-p-dioxins (log K_{oa} range 10.0 to 11.4) at three sampling sites attained values of 0.5, 0.9, and 2.0 for three sampling sites. These observations suggest that the air-SPMD boundary layer is rate limiting for the uptake of compounds with a log $K_{oa} > 8.5$. The uptake of compounds that are more volatile than the PRC could be partially or completely membrane controlled. The application of equation 11 for these compounds would likely result in the overestimation of their k_e values. This would not result in appreciable errors in the estimate of C_a, because the PRC usually has attained a significant degree of equilibrium, and the more volatile

compounds will have attained a larger degree of equilibrium. This means that the group 1-exp(-k_et) in equation 1 is close to one for these compounds anyway, and that the calculated C_a values are quite insensitive to uncertainties in k_e , and never exceed the estimates from the equilibrium model.

The purpose of the present study was to assess atmospheric concentrations of HCB and a number of PCBs along a height gradient (1600-2600 m) in the Pyrenees over a 1.5 year period, and to validate atmospheric sampling by SPMDs against sampling by HiVols.

Table 1. Sampling days and average temperatures (ºC) of the three sites and the average amounts in the SPMDs, the dissipation rate constants of PRC 155, sampling rates of PRC 155 and PRC 29, and the state of equilibrium of the studied compounds in the SPMDs.

		Sampling I	Sampling II	Sampling III
Period		25/3/2-18/6/2	18/6/2-15/1/3	15/1/3-25/6/3
Days		85	211	161
Average Ta (ºC)	Tuc (2600m)	-0,9	3,9	1,2
	Estany Redon (2250m)	2,6	5,8	4,0
	CRAM (1600m)	8,8	9,3	9,0
N_s (pg SPMD^{-1})	HCB	1120 (171)	3865 (461)	461 (114)
	PCB18	55 (30)	67 (20)	156 (10)
	PCB28	117 (18)	158 (43)	304 (243)
	PCB52	112 (26)	215 (38)	551 (314)
	PCB101	280 (84)	435 (107)	459 (149)
	PCB110	170 (65)	180 (35)	378 (72)
	PCB153	298 (148)	355(21)	293 (42)
	PCB138	147 (113)	276 (14)	287 (61)
	PCB180	89 (59)	76 (29)	107 (40)
$k_{e,CB155}$ (d^{-1})	Tuc (2600m)	0.0069 (23%)	0.0038 (16%)	0.0032 (12%)
	Estany Redon (2250m)	0.0077 (-)	0.0049 (13%)	0.0046 (2%)
	CRAM (1600m)	0.0084 (2%)	0.0048 (17%)	0.0064 (16%)
$R_{s,\,CB155}$ (m^3 d^{-1})	Tuc (2600m)	1,3	0,61	0,55
	Estany Redon (2250m)	1,3	0,75	0,72
	CRAM (1600m)	1,1	0,64	0,82
$R_{s,\,CB29}$ (m^3 d^{-1})	Tuc (2600m)	2,9	-	-
	Estany Redon (2250m)	2,5	-	-
	CRAM (1600m)	1,6	-	-
Equilibrium %	HCB	92	98	94
	PCB18	81	92	84
	PCB28	67	81	72
	PCB52	68	80	72
	PCB101	39	51	43
	PCB110	37	49	41
	PCB153	3,2	5,4	4,1
	PCB138	2,2	3,6	2,8
	PCB180	0,3	0,6	0,4

Materials and methods

SPMD-sampling. SPMDs were exposed in duplicate during 3 sampling periods of 85, 161 and 210 days, between March 2002 and June 2003 (Table 1) near the high mountain lake Estany Redon (42°38´33.5´´N; 0°46´12.7´´E; 2240m), in the central Pyrenees (Catalonia, Spain). They were analyzed for HCB and eight individual PCB congeners. Additional exposures were performed made simultaneously in the valley and on the mountaintop, close to the Centre of High Mountain Research (CRAM) at 1600m and near Tuc deth Port de Vielha at 2600m, in the vicinity of Estany Redon (Figure 1). All sites are characterized by their sub-alpine to alpine environments, with an average annual ambient temperature in 2002 of 3.7ºC and snow cover from November until May at Estany Redon and an average annual ambient temperature of 8.3ºC at 1600m.

The SPMDs (30 x 2.5 cm, wall thickness 70μm) were filled with 270 mg spiked triolein (Sigma, 95%). The triolein content was 21% (w/w) and the surface area to triolein volume ratio was 510 cm2/mL, which is slightly higher than for standard design SPMDs (20%, and 460 cm2/ml, respectively). The triolein was spiked with 40, 7, 7 ng of PCB4, PCB29 and PCB155, respectively. None of these PCBs were detected in the high-volume air samples (see below). To protect the SPMDs against direct sunlight and wind they were mounted inside a sampler, which consisted of an untreated wood pole with an upside-down zinc bucket that was closed off with a steel wire screen (maze width 8 mm). A similar sampler was used successfully in other studies (15). For each sampling period, two non-exposed SPMDs filled with spiked triolein where analyzed as blanks. The limit of quantification (LOQ) was calculated from the average blank value plus 3 x the standard deviation. Blank values of detected compounds were about 0.03-0.2ng per SPMD. LOQs were about 0.1-0.5ng per SPMD. Blank correction was applied to all samples.

The SPMDs were stored in closed glass bottles at –20ºC. During transport to and from the sampling sites, the bottles were stored at 0ºC for a couple of hours. Handling of SPMDs was done with pre-cleaned tweezers. After exposure, the exteriors of the SPMDs were wiped off with a paper tissue to remove eventually attached particles. After cutting off the triolein-free mounting loops, the SPMDs were extracted twice for 24h by soaking in 100 ml hexane:dichloromethane (DCM) (4:1 v/v) (Merck, Darmstadt, Germany). Internal standards, PCB30 and PCB209, were added at the beginning of the first extraction period. The analytical recovery was studied twice using SPMDs that contained PCB spiked triolein. Recoveries of 93±13% were observed for all compounds. The recoveries of the internal standards, PCB30 and PCB209 in the samples were 87±21% and 87±17%, respectively. For each series, 2 SPMDs were used as a control, to determine the initial concentrations of the PRCs. These SPMDs were processed together with the exposed SPMDs. PRC recoveries from the control SPMDs were 40±27% for PCB4 and 93±10% for PCB29 and PCB155, relative to the calculated spike levels.

All extracts were concentrated to 0.5 mL. Clean-up of the extracts was done using a column that was filled with 8 g silica (Pancreac, Spain) (5% H_2O), 8 g aluminum oxide (Fluka Type 507C,

Fluka AG, Switzerland) (5% H_2O), and 1 g Na_2SO_4 . The samples were eluted with 20 mL hexane, followed by elution with 20 mL hexane:DCM (19/1 v/v). The collect fraction was evaporated to 0.5 mL using vacuum rotary evaporation and further concentrated until 50 μL in iso-octane (Merck, Darmstadt, Germany) under a gentle nitrogen stream. Before injection, 25 μL of tetrachloronaphthalene was added to correct for variations in instrument sensitivity and sample volume. The samples were injected on a Hewlett-Packard 5890 Series II gas chromatograph equipped with an electron capture detector for the analysis of HCB and PCB congeners #18, #28, #52, #101, #110, #153, #138, #180. The GC was equipped with a fused silica capillary column DB5 (50 m x 0.25 mm i.d. x 0.25 μm film thickness; J&W Scientific, Folsom, CA). Nitrogen and helium were used as make up gas (60 mL min^{-1}) and carrier gas (0.33 mL min^{-1}), respectively. The oven temperatures were programmed from 100ºC (1 min) to 150ºC at 15ºC min^{-1}, following a heating of 4ºC min^{-1} until 240ºC (holding time 12 min.), and then to 300ºC at 4ºC min^{-1} with a final holding time of 10 min. Samples were injected in split/splitless mode at 280ºC. The detector temperature was 310ºC.

HiVol-sampling. The method of atmospheric sampling with the HiVol-sampler is fully described in Van Drooge et al. (4, 27). Briefly, samples and blanks were collected between November 2000 and June 2003 at Estany Redon using a high volume pump (HiVol) (MCV, S.A., Collbato, Catalonia, Spain) equipped with two plugs of polyurethane foam (PUF) and a glass fiber filter (GFF). Collected air volumes were between 120 m^3 and 280 m^3. After sampling, PUFs and GFFs were stored at 0ºC during transport to the laboratory. PUFs and GFFs were Soxhlet extracted for 24h in hexane and hexane:DCM (4:1 v/v), respectively. The extracts were concentrated to 1 mL by vacuum rotary evaporation and cleaned-up by column adsorption chromatography on 2 g of aluminum-oxide and elution with 8 mL hexane:DCM (1:2 v/v). The extracts were then concentrated in iso-octane to 50 μL under a gentle stream of nitrogen. Prior to injection, tetrachloronaphthalene was added to the vials as an injection standard. The same instrumental analysis procedure was used as for the SPMD extracts.

Table 2. Physico-chemical properties of analysed organochlorine compounds (at 25ºC).

		#4	#29	#155	HCB	#18	#28	#52	#101	#110	#153	#138	#180
logKow	(28)	4,9	5,6	7,0	5,5	5,6	5,8	6,1	6,4	6,3	6,9	7,0	6,9
logKsw	(19)	4,8	5,3	6,3	5,2	5,3	5,4	5,7	5,9	5,8	6,2	6,3	6,2
H (Pa/m^3 mol)	(21,29)	33,3	30,0	85,2	53,0	32,4	28,9	32,3	24,9	19,9	16,7	13,2	10,9
DHaw (kJ/mol)	(21,22)	42,0	41,0	27,0	49,0	42,0	41,0	27,0	29,0	29,0	79,0	79,0	149,0
LogKsa	*)	6,7	7,2	7,8	6,9	7,2	7,4	7,5	7,9	7,9	8,4	8,6	8,6
D_a (10^{-6} m^2/s)	(26)	5,1	4,9	4,3	5,1	4,9	4,9	4,7	4,5	4,5	4,3	4,3	4,2

*) calculated from Ksw and H

Physico-chemical properties. The required physico-chemical properties of the studied compounds are summarized in Table 2. The log K_{ow} values were obtained from Mackay et al. (28). Because no values or CB138 and CB180 are listed in this reference, the average value of hexaCB and heptaCB were chosen, respectively. The log K_{sw} values were calculated from the equation given by Booij et al. (18). Henry´s Law constants (H) for PCB and HCB were obtained from Dunnivant et al. (29) and from Ten Hulscher et al. (21), respectively. Water-air transfer enthalpies (ΔH_{aw}) were taken from Ten Hulscher et al (21) for HCB, and from Bamford et al. (22), adopting the average value for PCBs with the same number of chlorine atoms and the same number of ortho-chlorines. Diffusion coefficients (D_a) were calculated using the Fuller, Schettler & Gillings equation (26).

Ambient Temperature. Ambient temperatures (T_a) were obtained from the meteorological stations situated at Estany Redon (2250m) and at the Centre of High Mountain Research (CRAM) (1600m). Both stations are located in the same valley, near the sampling sites. At Estany Redon, the average T_a was calculated from measurements taken every 30 min. At CRAM, T_a was calculated from the daily minimum and maximum temperatures. Values of T_a of these sites were used to calculate the temperature lapse rates, this in order to estimate the T_a for the sampling sites at 2600m. For the three sampling periods the lapse rates were 1.0, 0.5 and 0.8 ºC per 100 m, respectively. The average T_a values are summarized in Table 1.

Results and discussion

Performance reference compounds. The amounts of CB4 were below the detection limit for all exposed SPMDs. CB29 was only detected in the SPMDs exposed during the first sampling period (85 days). In the other sampling periods CB29 was below the detection limit. The average retention of CB155 was 45% in exposed SPMDs, with a standard deviation of 10%. Dissipation rate constants (k_e) could therefore only be estimated for CB155 for all exposure period and for CB29 for the first exposure period. The k_e of CB155 for one of the SPMDs from the first sampling period at Estany Redon was exceptionally high (0.016 d^{-1}) compared to the estimated for other altitudes and exposure periods. This value was therefore excluded from the further calculations. No significant differences ($p>0.05$) in k_e estimates were observed among the different sampling heights for all three sampling periods. CB155 dissipation rate constants for the second and third sampling period were virtually the same at all sites, while the average k_e for the first sampling period is significantly higher ($p<0.0001$) compared to periods 2 and 3 (Table 2). The coefficients of variation among the duplicates ranged between 2 and 23%. The dissipation rate values of CB155 were used to calculate the sampling rate (R_s) of compounds with the same physico-chemical properties as CB155, using equation 5. The $R_{s,CB155}$ for the first sampling period were higher than in the other two samplings by a factor of 1.8 (Table 2). The higher sampling rates during the first period are not likely to be temperature-related, because temperature differences were larger among sampling sites

(~ 10 °C) than among sampling periods (~ 3 °C), but no differences in R_s among sites were observed.

With boundary-layer controlled uptake, increasing wind speed may cause an increase in sampling rates. Wind speeds normally increases with altitude (30), but no increase of $R_{s,CB155}$ with altitude was observed. It is there for not clear what the reason may be for the difference in sampling rates between the first sampling period and the other two.

The range of $R_{s,CB155}$ values found in this study are smaller than the wintertime values of penta- and hexachlorobiphenyls observed by Ockenden et al. (14). After applying a correction for the differences in surface area (152 cm^2 versus 460 cm^2), the present sampling rates are a factor 3.2 smaller than those observed by Ockenden et al. (14). Differences in wind speed may be responsible for these differences in sampling rates. Another explanation is related to uncertainties in the K_{sa} values used to calculate the sampling rates in the present study. Errors in the K_{sa} values may arise from uncertainties in the log Kow values used to calculate the SPMD-water partition coefficient. A 0.2 log unit increase in log Kow would cause the sampling rate estimates to increase by a factor of 1.4. Uncertainties in the Henry's Law constants for CB155 are a similar source of error. For the first sampling period, additional sampling rate estimates could be made using the dissipation of CB29. R_s values based on the dissipation of CB29 were higher than CB155-based sampling rates by a factor of 1.9. This difference is most likely caused by the lack of reliable experimental K_{sa} values for these PRCs.

Equilibrium of OCs in SPMDs. The dissipation of CB4 (log K_{sa} = 6.7) was complete, and CB29 (log Koa = 7.2) had dissipated more than 93% in the first exposure period (85 d). This implies that equilibrium was complete (equilibrium sampling mode) for all compounds with log K_{sa} values smaller than ~ 7.2 (HCB, PCB18). The dissipation of CB155 (log K_{sa} = 7.8) was 55%, indicating that compounds with similar log K_{sa} values (PCB101, PCB110) were neither in the equilibrium sampling mode, nor in the kinetic sampling mode, but in the intermediate mode instead. The use of equation 1 for calculating the atmospheric concentrations accounts for the partial attainment of equilibrium for these compounds. The log K_{sa} values of PCB28 (~7.4) and PCB52 (~ 7.5) are larger than the log K_{sa} of CB29, and smaller than the log K_{sa} of CB155, which means that the extent of equilibrium attainment is somewhere between 55 and 100%. Assuming that the degree of equilibrium can be estimated by interpolation over this narrow log K_{sa} range, the equilibrium attainment of CB28 and CB52 would be ~ 80% and ~ 74%, respectively. The calculation method proposed in the introduction (application of equation 1 and k_e estimation using equation 11), yields equilibrium estimates between 67 and 81% for CB28 and 68 to 80% for CB52 (Table 1). These values are clearly consistent with the equilibrium percentages obtained by the interpolation method. This indicates that the proposed model may be applied for compounds with log K_{sa} values smaller than that of the PRC. We would like to stress that we do not imply that the uncertainties in the method is in the range of a few percent for the low K_{sa} range. Instead, the errors involved are of the

same order as the errors in the K_{sa} values, which may attain values of up to 0.3 log units, depending on the accuracy of the parameters log Kow and H.

Atmospheric concentrations. SPMD-based atmospheric concentrations are shown in Figure 2 for all altitudes and sampling periods. The concentrations of the PCB congeners are very similar for all three sampling periods. There is a slight decrease of the atmospheric levels with increasing altitude in sampling I, but in general the concentrations of the analyzed compounds are in the same range for the three sampling sites.

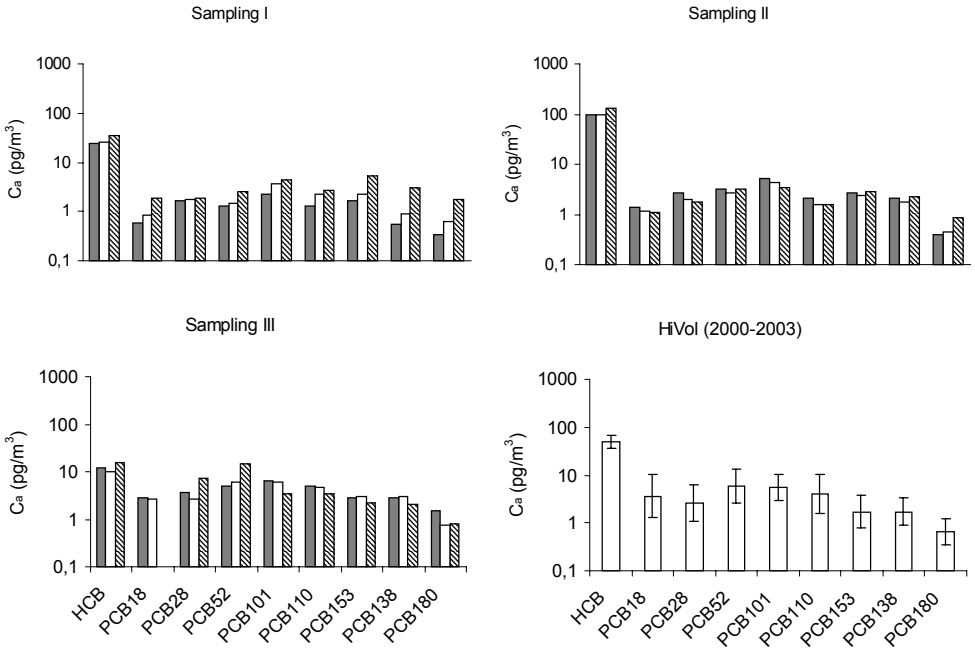

Figure 2. SPMD-derived concentrations for sampling periods I (top), II (middle), and III (bottom) measured at 2600m (filled bars), 2240 m (open bars) and 1600m (hatched bars) as well as the average HiVol-derived atmospheric OC concentrations between 2000 and 2003 (N=20).

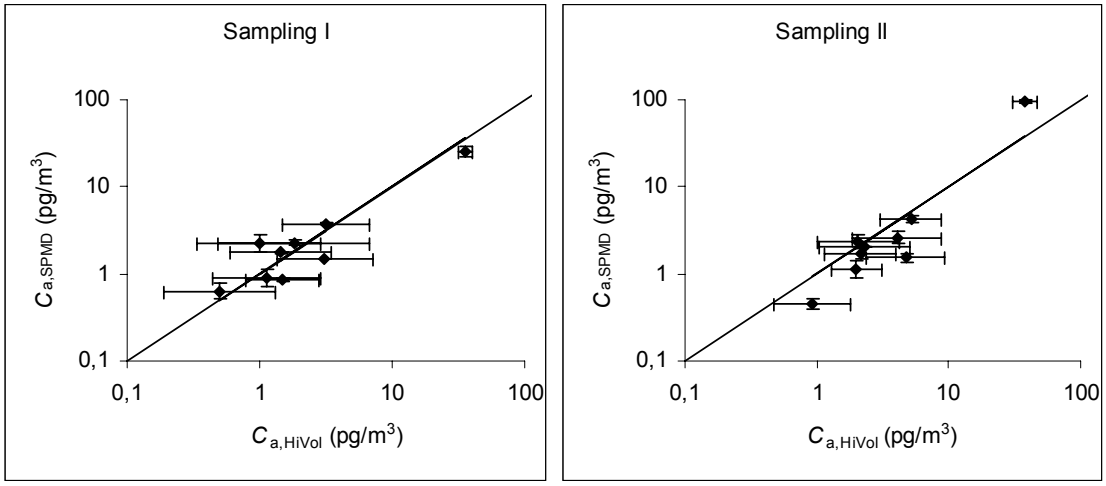

Figure 3. Comparison of average atmospheric log concentrations (pg m^{-3}) obtained from the SPMD and HiVol-sampling at Estany Redon (2250m)

Comparison with HiVol data. HiVol samples were taken at the beginning an at the end of exposure periods I and II near Estany Redon. The SPMD-based atmospheric concentrations ($C_{a,SPMD}$) are plotted versus the mean HiVol-derived concentrations ($C_{a,HiVol}$) in Figure 3. The ratio $C_{a,SPMD}$ / $C_{a,HiVol}$ attained values between 0.4 and 3.1, with a geometric mean of 1.2. The error bars on the HiVol-based concentrations reflect the high time-variability associated with this technique (factor of ~ 2.1). The variability among $C_{a,SPMD}$ duplicates was a factor of ~ 1.1. The good correspondence between the two techniques is better than one would expect, considering the uncertainties in the log K_{sa} values that are needed to obtain $C_{a,SPMD}$ estimates. The similarity in C_a values obtained by both methods also indicates that reliable estimates of atmospheric concentrations of PCBs and HCB can be obtained by SPMD deployments in remote areas using the PRC method.

Acknowledgements.

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Article 7.

PERSISTENT ORGANOCHLORINE COMPOUNDS IN SOILS AND SEDIMENTS OF EUROPEAN HIGH ALTITUDE MOUNTAIN LAKES

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Persistent organochlorine compounds in soils and sediments of European high altitude mountain lakes

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Abstract

The composition of persistent organochlorine compounds (OC) in soils and sediments from two high altitude European mountain lakes, Redon in the Pyrenees and Ladove in the Tatra mountains, has been studied. Sediment cores from two additional lakes in the Tatra mountains, Starolesnianske Pleso and Dlugi Staw, have also been examined. DDTs (1.7–13 ng g^{-1}) were the most abundant OC in soils followed by total polychlorobiphenyls (PCBs; 0.41–1.5 ng g^{-1}) and hexachlorobenzene (HCB; 0.15–0.91 ng g^{-1}). In sediments, the dominant OC were also DDTs (3.3–28 ng g^{-1}) and PCBs (2.3–15 ng g^{-1}). These concentrations are low, involving absence of major pollution sources in these high mountain regions.

The downcore OC profiles in soils and sediments were similar but higher concentrations and steeper vertical gradients were observed in the latter. Radiometric determinations showed absence of significant OC transport from catchment to lake. The sediment–soil difference points therefore to a better retention of the OC load in sediments than soils which may be related to the low temperatures that are currently encountered at the bottom of the lake water column and the depletion of sediment bioturbation in these cold environments.

Significant qualitative changes in the soil PCB distributions are observed downcore. These involve a dominance of the high molecular weight congeners in the top core sections and those of lower weight (i.e. less chlorinated) in the bottom. Anaerobic dechlorination of higher molecular weight congeners occurring in microsites, e.g. as observed in flooded or poorly drained soils, could be responsible for these changes. This process could be concurrent to bioturbation.

Keywords: Organochlorine compounds; High mountains; Soils; Lacustrine sediments; Trace chemical pollution in remote environments

1. Introduction

An important increase of organochlorine compounds (OC) such as polychlorobiphenyls (PCBs), DDTs, hexachlorocyclohexanes (HCH) and hexachlorobenzene (HCB) in the global environment has been observed over the last century as a consequence of their extensive use since the Industrial Revolution (Keith and Telliard,

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1979; Eisenreich et al., 1989; Alcock et al., 1993; Sanders et al., 1994). In the seventies, concern over their potential toxicity and high persistence, led to the implementation of many regulations for their restricted use or banishment. Over the last decade, scientific interest has been focused on the study of historic inputs in soil/sediments for the evaluation of the success of these international environmental policies (Rapaport and Eisenreich, 1988; Oliver et al., 1989; Sanders et al., 1995; Wong et al., 1995; Muir et al., 1996; Krauss et al., 2000). However, evaluation of long-term changes in remote sites has been barely considered.

Environmental contamination with persistent OC may be related to point sources (industrial discharges and waste plant effluents) or, more frequently, to diffuse sources (atmospheric transport and deposition) which are the major pathway for the transfer of these persistent organic pollutants to remote sites.

In principle, the accumulation of OC in soils and sediments of remote sites should provide similar downcore records. However, soils and sediments possess different microenvironmental conditions affecting air and water exchange and post-depositional processes. Comparison of the accumulation patterns of OC in these two environmental compartments is therefore a pre-condition for an integrated understanding of the pollution load of these compounds in remote sites. High mountain areas are ideal environments for this purpose since both compartments are under the same atmospheric precipitation fluxes.

In this respect, it should be mentioned that a priori soils contribute to lake sediments but not the reverse. Thus, the terrestrial pathway is different between the two reservoirs. In the present study, radiometric measurements have been performed in order to ascertain the specific links between them.

The Pyrenees are a mountain range where moderate OC pollution concentrations have been recorded (Grimalt et al., 2001). Lake Redon (42°38′34″N, 0°46′13″E; 2240 m above sea level; Fig. 1) is the largest high mountain lake in this area (24 ha) and has been used as reference lake for many environmental studies (Catalan, 1988, 1992). One lake sediment core and two soil cores collected near the lake are considered in the present study.

The Tatra mountains are situated in central Europe. Sediment cores from Ladove Lake (49°11′03″N, 20°09′46″E; 2057 m), Starolesnianske Pleso (49°10′N,

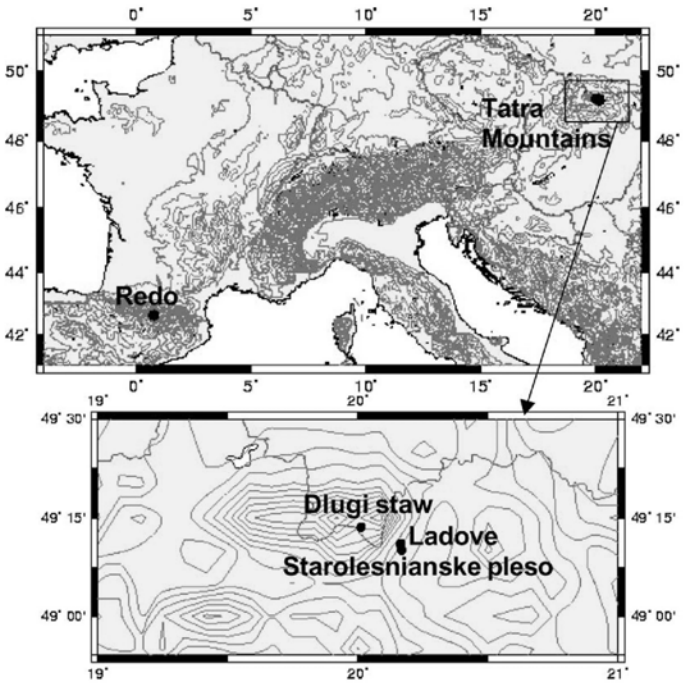

Fig. 1. Maps showing the location of the lakes considered for study.

20°10′E; 2000 m) and Dlugi Staw (49°13′36″N, 20°0′39″E; 1783 m) are considered for study (Fig. 1). The two former lakes are situated at less than 2 km of distance. Two soil cores were analyzed near Ladove Lake.

To the best of our knowledge, this is the first study comparing downcore distributions of OC in soils and lake sediments, particularly in high mountain areas.

2. Materials and methods

2.1. Materials

Residue analysis-grade *n*-hexane, dichloromethane, isooctane, methanol and acetone were from Merck. Anhydrous sodium sulfate for analysis was also from Merck. Neutral aluminum oxide type 507C was from Fluka AG. Cellulose extraction cartridges were from Whatman Ltd. Aluminum foil was rinsed with acetone and let dry at ambient temperature prior to use. The purity of the solvents was checked by gas chromatography-electron capture detection (GC-ECD). We detected no significant peaks for any of the reagents. Aluminum oxide, sodium sulfate and cellulose cartridges were cleaned by Soxhlet extraction with hexane:dichloromethane (4:1, v/v) during 24 h before use. The purity of the cleaned reagents was checked by ultrasonic extraction with *n*-hexane:dichloromethane (4:1; 3×20 ml), concentration to 50 μl and analysis by GC-ECD. No interferences were detected. Sodium sulfate and aluminum oxide were activated overnight at 400 and 120 °C, respectively.

2.2. Sampling

Sediment samples were taken in the deepest points of the lake using a gravity coring system (Glew, 7.5 cm diameter, 30 cm long). A 7 cm (diameter) × 20 cm (long) stainless steel cylinder was used for soil core collection. All soils were taken in the lake catchment areas. Soil and sediment cores were immediately divided in sections of 2 and 0.5 cm, respectively (0.3 and 0.25 cm in the case of Redon and Ladove sediments, respectively), and stored in pre-cleaned aluminum foil at −20 °C until analysis.

2.3. Analysis

The following OC were determined in the soil cores: HCB, α-HCH, β-HCH, γ-HCH, δ-HCH, DDTs and PCB congeners #18, 28, 52, 70, 90, 101, 105, 110, 118, 123, 132, 138, 149, 153, 158, 160, 180, 194 and 199. In sediments, HCB, DDTs and the polychlorobiphenyl congeners #28, 52, 90, 101, 118, 123, 138, 149, 153, 160 and 180 were determined. In addition, PCB congeners 70, 105, 110, 132, 158, 194 and 199 were also analyzed in the sediment core of Lake Ladove.

2.4. Sample extraction

Soils were weighed into a Whatman Soxhlet cellulose thimble. About 1:1 w/w sodium sulfate were mixed with the soil samples in order to improve Soxhlet extraction by water removal. Prior to extraction, samples were spiked with PCB congeners #30 and 209 which were used as surrogate standards. Samples were extracted with hexane:dichloromethane (4:1) for 18 h. All extracts were first concentrated by rotary vacuum evaporation to 3–5 ml and subsequently eluted through an anhydrous sodium sulfate column. After rotary vacuum evaporation to ∼0.5 ml, the extracts were fractionated on a neutral aluminum oxide column (2 g). The OC were eluted with 8 ml of hexane:dichloromethane (9:1).

For sediments, about 0.1–1 g of wet sediment was extracted by sonication with methanol (1×20 ml; 20 min) in order to separate most of the interstitial water. The subsequent extractions were performed with (2:1, v/v) dichloromethane–methanol (3×20 ml; 20 min). All extracts were combined and spiked with PCB congeners #30 and 209. Then, they were vacuum evaporated to 10 ml and hydrolyzed overnight with 20 ml of 6% (w/w) KOH in methanol. The neutral fractions were recovered with *n*-hexane (3×10 ml), vacuum evaporated until dryness, and fractionated by adsorption column chromatography as described for the soil samples.

Activated copper (∼1 g) was added to soil and sediment organochlorine fractions for removal of sulfur-containing compounds. This copper powder was removed by filtration though glass wool and rinsed with *n*-hexane. Elution solvent and rinses were concentrated to 50 μl in isooctane after rotary vacuum and nitrogen stream evaporation.

2.5. Instrumental analysis

The extracts were injected into a Hewlett Packard 5890 Series II GC-ECD. An HP-5 fused silica capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) coated with 5% phenyl 95% methylpolysiloxane was used for the analyses. The oven temperature program started at 100 °C (holding time 1 min), increased to 120 °C at 20 °C min^{-1}, to 240 °C at 4 °C min^{-1} (holding time 12 min) and finally to 300 °C at 4 °C min^{-1} (holding time 10 min). Injector and detector temperatures were 280 and 310 °C, respectively. Helium and nitrogen were used as carrier (0.33 ml min^{-1}) and make-up (60 ml min^{-1}) gases, respectively. Compound identification was confirmed by GC coupled to mass spectrometry in the chemical ionisation mode and

negative ion recording (Fisons 8000 Series, Mass Selective Detector 800 Series).

2.6. Quantification

Solutions of tetrachloronaphthalene and octachloronaphthalene were added to the vials prior to injection. Calibration curves (detector response vs amount injected) were performed for each compound to be quantified. The range of linearity of the detector was evaluated from the curves generated by plotting detector signal/amount injected vs amount injected. All measurements were performed in the ranges of linearity found for each compound. In some cases, the samples were rediluted and reinjected for fitting within the linear range of the instrument. The quantitative data were corrected for surrogate recoveries.

2.7. Total organic carbon

Soil and sediment samples were extracted with HCl 3N to remove inorganic carbon. Subsequently, they were cleaned with Milli-Q water until neutral pH (7 ± 0.2) and dried at 60 °C. The determination of TOC was performed by flash combustion at 1025 °C followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. The limit of detection was 0.1%.

2.8. Radiometric dating

Sediment and soil samples were analyzed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby et al., 1986). ^{210}Pb was determined via its gamma emissions at 46.5 keV and ^{226}Ra by the 295 and 352 keV γ-rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662 and 59.5 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy γ-rays within the sample (Appleby et al., 1992). Supported ^{210}Pb activity was assumed to be equal to the measured ^{226}Ra activity. Unsupported ^{210}Pb activity was calculated by subtracting supported ^{210}Pb from the measured total ^{210}Pb activity. ^{210}Pb radiometric dates were calculated using the CRS and CIC dating models (Appleby and Oldfield, 1978) where appropriate and validated where possible against the 1986 and 1963 depths determined from the ^{137}Cs/^{241}Am stratigraphic records.

3. Results and discussion

The lakes considered for study are situated above the local tree line, they are oligotrophic (median total phosphorous <4.1 $\mu g l^{-1}$) and remain ice-covered for long periods during the year. Three dominant types of land cover are found in the lake catchment, dry alpine meadows, moraines and solid rock. Among these, the former were selected for study. Soils in the dry alpine meadows are mostly undeveloped (e.g. leptosol, podsol and histosol) with average mineral horizons of about 33 cm thickness and shallow organic matter horizons (5–17 cm, average 4 cm). These soils are covered by grass in summer and under snow during the cold months (Catalan, 1988). All pollution is presumably derived from atmospheric transport since the lakes are free from local anthropogenic sources.

3.1. Total organic carbon

TOC is generally higher in the soil than in the sediment cores. In Redon Lake it ranges between 16% and 34% (average values 19% and 28% in the two cores) in the soils and between 2% and 5% in the sediments (average 3.6%) (Table 1). The core sections of soils and sediments in the Tatra mountains show smaller differences. Thus, TOC range between 6% and 35% (average values 8.6% and 15% in the two cores) in Ladove soils and between 9% and 14% (average values 9.2% and 12.5%) in the sediments from the lakes in the Tatra mountains (Table 1).

In contrast to other studies (Ribes et al., 2002) no significant correlation ($P > 0.05$) was found between the concentrations of TOC and OC in the soils of these two lakes (Table 1). Therefore, soil concentrations have not been TOC normalized.

3.2. Organochlorine compounds in soils

Total average PCB levels range between 0.41–0.68 and 0.87–1.5 $ng g^{-1}$ in Redon and Ladove soils, respectively (Table 1). All concentrations refer to dry weight unless otherwise stated. The concentrations of these soils from high mountain lacustrine catchments are similar to those found in woodland regions of Germany (0.2–4.8 $ng g^{-1}$; Krauss et al., 2000) and Austria (0.2–7.5 $ng g^{-1}$; Weiss et al., 1998) and rural areas of Thailand (1.1–6.2 $ng g^{-1}$; Thao et al., 1993). In contrast, Redon and Ladove soil concentrations are low in comparison to those reported in industrial areas of Austria (6.4–95 $ng g^{-1}$; Weiss et al., 1994) and Poland (4.6–3400 $ng g^{-1}$; Falandysz et al., 2001), rural sites of UK and Norway (1.2–2000 $ng g^{-1}$; Creaser et al., 1989; Alcock et al., 1993; Sanders et al., 1995; Lead et al., 1997), Germany (8.4–60 $ng g^{-1}$; Wilcke and Zech, 1998) and Brazil (27–49 $ng g^{-1}$; Wilcke et al., 1999) or even in woodland re-

Table 1
Total organic carbon (TOC, %) and concentrations of the main organochlorine compound groups (ng g^{-1} dw) in the sediment and soil cores of the high altitude lakes considered in this study

	Redó			Ladove			Starolesnianske Pleso	Dugli Staw
	Sediment	Soil (A)	Soil (B)	Sediment	Soil (A)	Soil (B)	Sediment	Sediment
TOC	3.6[a]	28	19	9.2	15	8.6	12.5	9.2
'	(5.1[b]–1.7[c])	(34–24)	(33–18)	(14–9.1)	(35–5.8)	(11–8.8)	(14–13)	(10.5–8.9)
HCB	0.18	0.15	0.91	1.3	0.23	0.33	4.2	1.6
	(1.1–0)	(0.29–0.004)	(3.4–0.013)	(1.1–0)	(0.40–0.06)	(0.37–0.08)	(11–0.81)	(4.5–0)
HCH	–	0.08	0.19	–	0.28	0.49	–	–
		(0.29–0.007)	(0.44–0.016)		(0.80–0.13)	(0.46–0.80)		
DDT[d]	3.3	1.7	3.4	12	4.5	13	28	25
	(15–0.27)	(2.9–0.07)	(6.9–0.03)	(1.0–1.4)	(10–0.42)	(37–0.26)	(54–1.3)	(43–2.7)
PCB[e]	2.3	0.41	0.68	15	1.5	0.87	15	10
	(7.2–0.74)	(0.33–0.46)	(0.72–0.20)	(5.4–2.7)	(5.1–1.8)	(2.8–0.5)	(32–3.1)	(44–0.45)

[a] Average concentration value of the whole core.
[b] Concentration of the upper section.
[c] Concentration of the bottom section.
[d] Sum of DDT and DDE.
[e] Sum of congeners #28–31, 52, 90–101, 118, 153, 138 and 180.

gions of Norway (5.3–30 ng g^{-1}; Lead et al., 1997) and USA (7.5–250 ng g^{-1}; Smith et al., 1993).

Average total DDTs (4,4′-DDE + 4,4′-DDT) are 1.7–3.4 ng g^{-1} and 4.5–13 in Redon and Ladove soils, respectively (Table 1) which is lower than concentrations reported in industrial/urban areas from Germany (500–400 000 ng g^{-1}; Wilken et al., 1994) and Poland (8.6–2400 ng g^{-1}; Falandysz et al., 2001) or woodland regions of USA (2.1–270 ng g^{-1}; Smith et al., 1993) but in the same order of woodland regions from Austria (<22 ng g^{-1}; Weiss et al., 1998).

Total HCH, average values of 0.08–0.19 and 0.28–0.49 ng g^{-1} in Redon and Ladove soils, respectively, (Table 1) are also low, e.g. concentrations reported in urban/industrial areas of Poland range between 0.36 and 110 ng g^{-1} (Falandysz et al., 2001) and in woodland regions of Austria between 0.6 and 6.6 ng g^{-1} (Weiss et al., 1998). γ-HCH dominates over α-HCH in the soils of Redon Lake whereas the α-isomer is dominant in the soils of Ladove Lake (Figs. 3 and 4). The difference between the two lakes probably reflects the historic use of this pesticide in the pure form or as technical mixtures containing high proportions of the α-isomer, respectively. At present, only pure lindane (γ-HCH) is approved for use (Harner et al., 1999).

Total HCB exhibit average values of 0.15–0.91 and 0.23–0.33 ng g^{-1} in Redon and Ladove soils, respectively, (Table 1). These concentrations are again lower than soil values reported in urban/industrial areas of Germany (100–1300 ng g^{-1} ; Wilken et al., 1994) and Poland (0.19–30 ng g^{-1}; Falandysz et al., 2001) but in the same order than in woodland regions of Austria (<1.9 ng g^{-1} ; Weiss et al., 1998).

These low concentrations suggest the absence of major pollution sources in these high mountain regions. They are also much lower than those reported for total PCBs and DDTs in mountain soils located near to industrial sites such as the Giant Mountains (Czech-Polish border) where concentration ranges of 5–140 and 20–5100 ng g^{-1}, respectively, have been found (Holoubek et al., 1994, 1998). In contrast, the concentrations of HCB in the soils of these high mountain lakes and the Giant Mountains, 0.47–48 ng g^{-1}, are more similar than for PCBs and DDTs (Holoubek et al., 1994, 1998).

In all cases except one, HCB in Redon soil B (Table 1), the concentrations of OC are higher in the soils from the lakes in the Tatra mountains than in Redon. This likely reflects the influence of higher use and production of these compounds near the Tatra region. Thus, high levels of HCH (0.36–110 ng g^{-1}), DDTs (8.6–2400 ng g^{-1}) and PCBs (4.6–870 ng g^{-1}) have been reported in cities from southern of Poland due to industrial activity (Falandysz et al., 2001). Furthermore, total PCB soil concentrations ranging between 1.5 ng g^{-1} (agriculture fields) and 53 mg g^{-1} (asphalt/gravel mixing plants) have been observed in north Slovakia as a consequence of 25 years in the manufacture of PCBs (Kocan et al., 2001).

Despite no direct sources of these OC are found nearby the lakes, it seems clear that air masses travelling up to the Tatra mountains carry higher amounts of these pollutants than those arriving to the Pyrenees. At these latitudes westerlies are generally dominant which involves that air arriving to the Tatras will pass over central continental areas whereas that reaching the Pyrenees may often come directly from the Atlantic ocean.

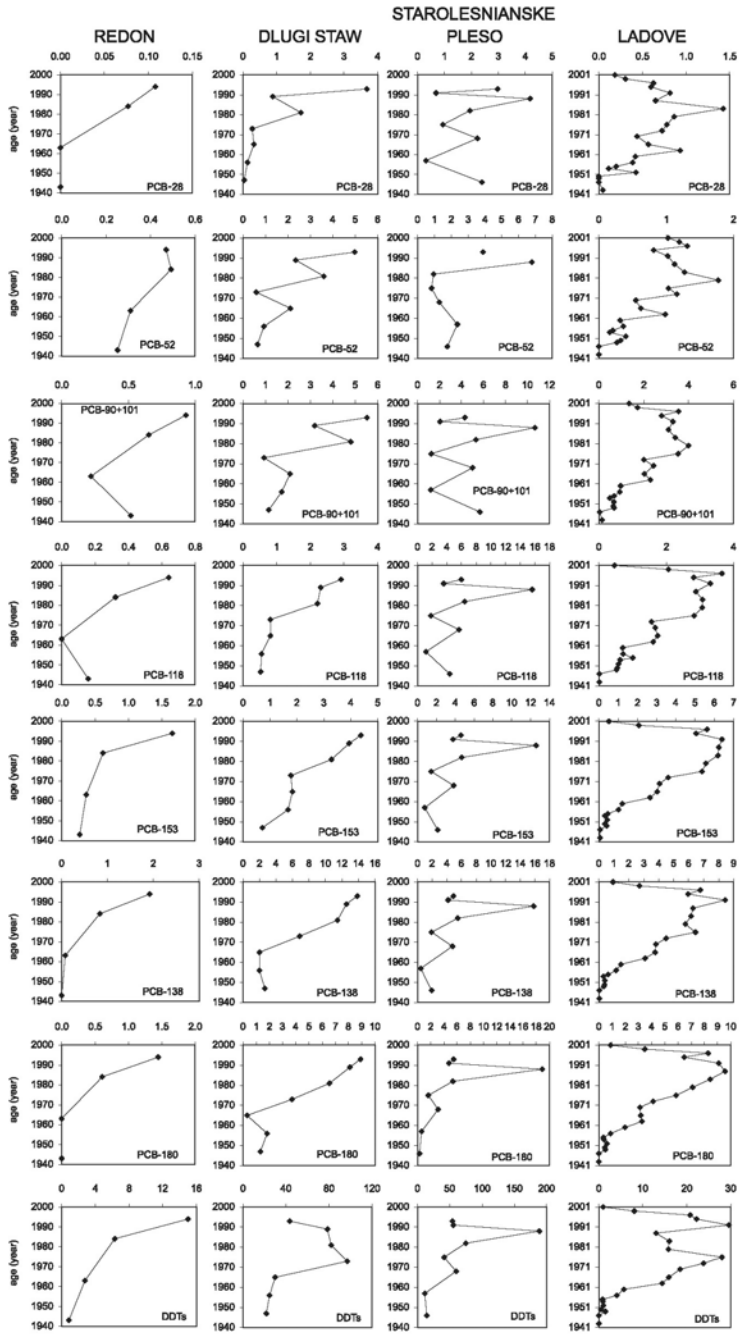

Fig. 2. Time scales of the concentrations of the major PCBs and DDTs (4,4′-DDE + 4,4′-DDT) determined from the sediment cores analyzed in Redon, Dlugli Staw, Starolesnianske Pleso and Ladove Lakes.

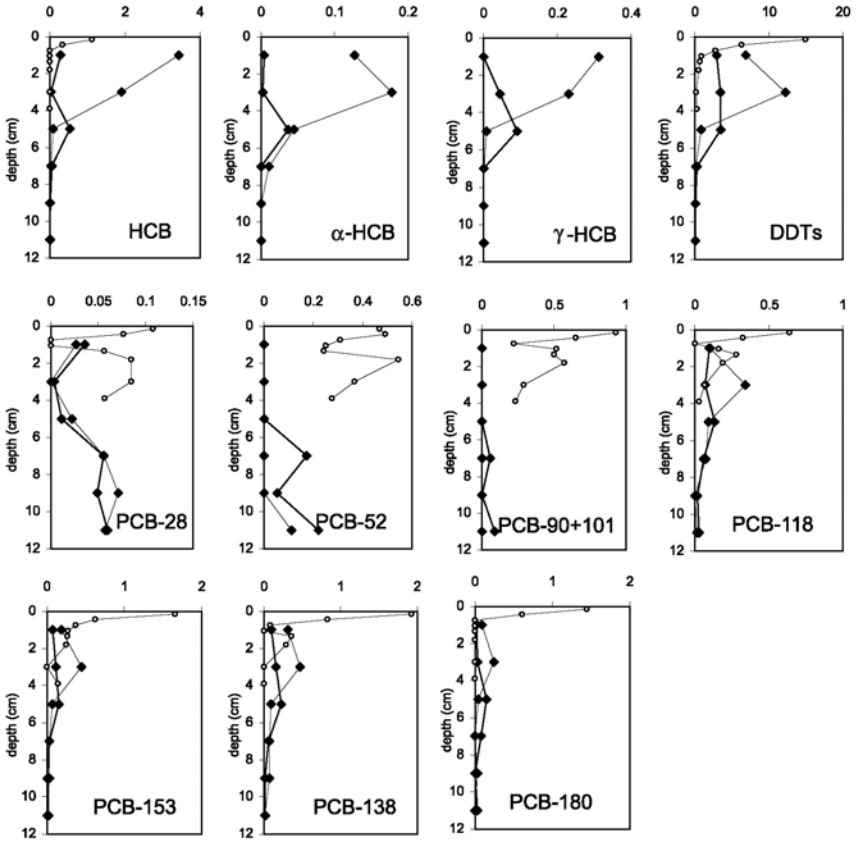

Fig. 3. Downcore graphs of the main OC found in the soils (◆) and sediments (○) of Redon Lake. Concentrations in $ng\,g^{-1}$ dry weight. The plots only compare the vertical structure of OC in soils and sediments, not involving temporal correspondences between the same depth levels.

3.3. Organochlorine compounds in sediments

The average PCB concentrations are higher in the sediment than in the soil cores in all cases (Table 1), 3–6 times higher in Redon and 10–20 times higher in Ladove. Average HCB concentration is also higher in the sediments than in the soils of Ladove Lake (about 5 times higher). However, in Redon Lake the average concentrations are four times higher in one soil core than in the sediment.

Average total DDT concentrations exhibit the lowest differences between soils and sediments. In both lakes, there is one soil core exhibiting similar concentrations than the sediment and the other soil core has lower values.

Radiometric measurements in soils and sediments show that there is little transport of fallout radionuclides from the catchment to Lake Redon and essentially none in Lake Ladove. Average ^{210}Pb flux in soil and sediment cores of Lake Redon was 286 ($n = 5$) and 182 ($n = 7$) $Bq\,m^{-2}\,y^{-1}$, respectively, and in soils and sediments of Lake Ladove it was 154 ($n = 5$) and 106 ($n = 5$) $Bq\,m^{-2}\,y^{-1}$, respectively. Thus, the generally higher concentrations of OC in sediments than in soils cannot be explained by soil erosion into the lakes.

Leaching, i.e. OC extraction from soils by percolating water, is also another hypothetical pathway for the transfer of these compounds from catchment. However, the high octanol–water partitioning coefficients, K_{OW}, of these OC (generally $\log(K_{OW}) > 10^4$) point to the preferential retention of these compounds in soil organic matter than leached to the lake. On the other hand, the differences cannot be explained by higher affinity of OC to organic matter since soils exhibit larger TOC than sediments in most cases (Table 1).

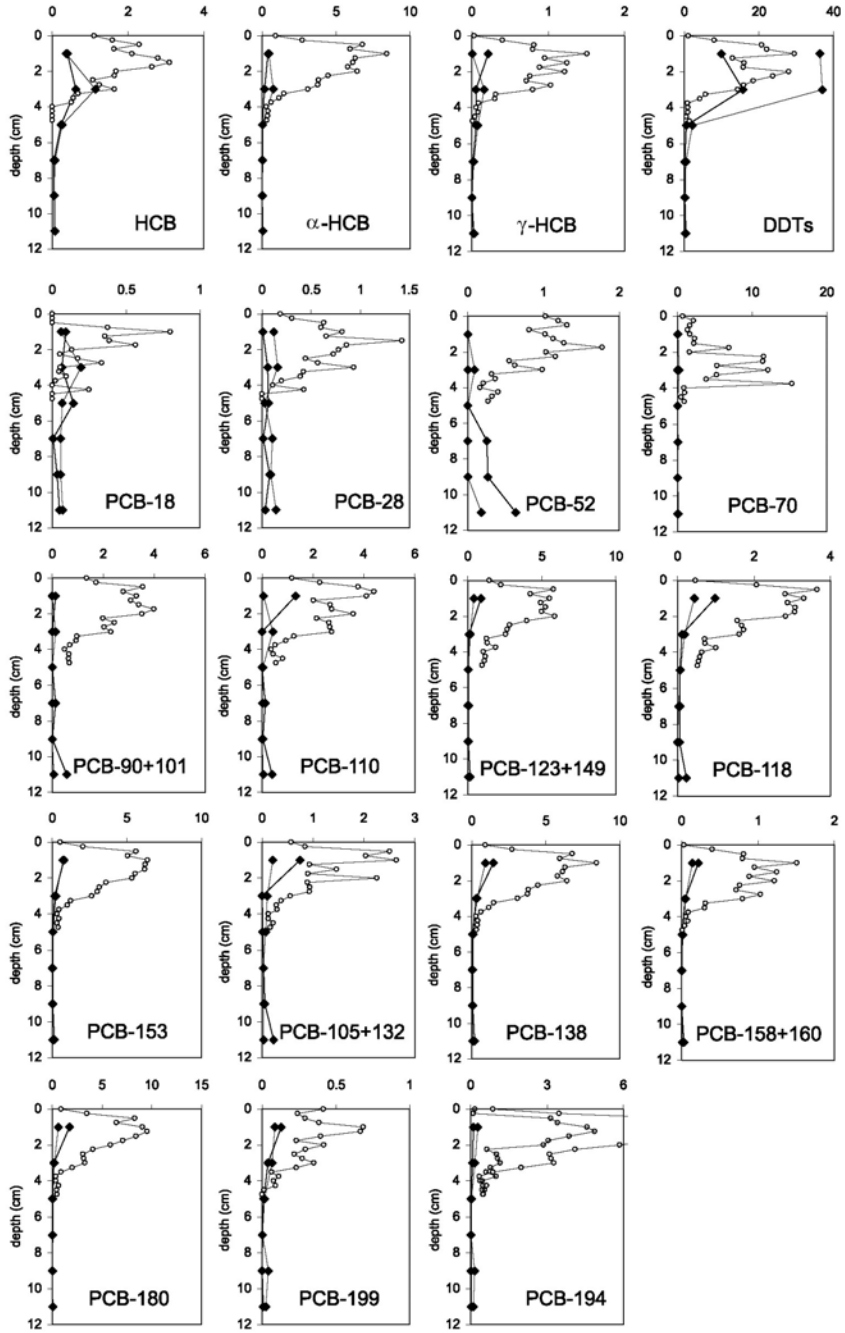

Fig. 4. Downcore graphs of the main OC found in the soils (◆) and sediments (○) of Ladove Lake. Concentrations in ng g $^{-1}$ dry weight. The plots compare vertical soil and sediment OC structures as indicated in Fig. 2.

Table 2
Dated sediment cores included in this study

Redo		Dugli Staw		Starolesnianske Pleso		Ladove			
Depth (cm)	Age (year)	Depth (cm)	Age (year)	Depth (cm)	Age (year)	Depth (cm)	Age (year)	Depth (cm)	Age (year)
0.15	1994	0.25	1992	0.25	1992	0.25	1999	2.50	1970
0.45	1984	0.75	1985	0.75	1990	0.50	1997	2.75	1966
0.75	1963	1.25	1977	1.25	1985	0.75	1995	3.00	1963
1.05	1943	1.75	1969	1.75	1979	1.00	1992	3.25	1960
1.35	1932	2.25	1961	2.25	1972	1.25	1988	3.75	1955
1.65	1916	2.75	1952	2.75	1963	1.50	1984	4.0	1954
2.85	1886	3.25	1940	3.75	1939	1.75	1980	4.5	1950
3.75	1842	3.75	1927	4.25	1925	2.00	1976	4.75	1949
		4.25	1914	4.75	1912	2.25	1973	5.00	1947

Having in mind the low catchment to lake transfer and that a priori both soils and sediments are under the same OC input, the OC concentration differences between the two reservoirs could be explained by higher retention efficiencies of the later than the former. Thus, the lake water column must essentially impede revolatilization to the atmosphere after deposition instead of obstructing air-to-sediment transfer. In this respect, lake bottom water temperatures are approximately constant at 4 °C in all seasons whereas soil temperatures have a strong seasonal variability reaching values higher than 10 °C in the warm periods (Catalan, 1992). The higher temperatures in the soils may enhance bioturbation in the warm periods and volatilization back to the atmosphere after deposition.

3.4. Vertical profiles in the lake sediments

Radiometric analysis showed that all lake sediment cores selected had rather uniform sedimentation (Fig. 2). No hiatus or periods of mixing were observed in the vertical structure of the recovered sediments. The average sedimentation rates of the sediment cores studied were 0.024, 0.054, 0.084 and 0.10 $cm\,y^{-1}$ for Redon, Dlugi Staw, Starolesnianske Pleso and Ladove. These rate differences and the core sectioning for analysis provide vertical OC profiles with different time resolutions at each site (Table 2).

The best time resolved OC trend is the one for Ladove Lake where biannual resolution is achieved in most core sections. The time trend of the major PCBs found in this core, #101, 118, 153, 138 and 180 defines a period of highest concentration between 1976 and 1997 (Fig. 2). Thus, despite the restriction of these compounds in the eighties there is no decline in the input of these compounds to this lake until later than 1997. The time-profile also shows two additional periods of increase, one between 1949 and 1957 when levels increase from below limit of detection to some small concentrations (below 1 $ng\,g^{-1}$ per individual PCB congener) and a second between 1963 and 1970 (about 3 $ng\,g^{-1}$ per individual PCB congener). These two periods probably reflect the historical use of PCBs in Europe which started to have significant exploitation after the Second World War.

Total DDTs in Ladove sediments exhibit a temporal pattern that is also showing concentration increases that started after the Second World War and arrive to maxima in 1976 (Fig. 2). This increase is also showing some steps but in general is more continuous and steep for the period between 1955 and 1976. After 1976 there is a significant drop in concentrations down to less than half the 1976 values between 1978 and 1990. However, there is a second maximum between 1992 and 1997 which likely reflects either a new period of use of DDTs in some parts of Europe or some remobilization of these compounds stored in some environmental compartment that produced a major second DDT pulse. As in the case of PCBs, after 1997 there is a strong decrease in the concentrations of these compounds in Ladove sediments.

The temporal concentration patterns of PCBs and DDTs in the other lakes of the Tatra mountains, Dlugi Staw and Starolesnianske Pleso, roughly agree with those in Ladove (Fig. 2). However, the temporal resolution is lower. Thus, less details are observable in the concentration changes.

The sediment core from Redo Lake is the one sampled at least time resolution (least sedimentation rate). In general it shows that the highest concentrations of both PCBs and DDTs correspond to the most recent section examined which, on average, is dated in 1994.

Overall, the cores show a concentration time dependence which is consistent with the known history of use of these compounds in Europe. Thus, they provide a reference material which can be used for comparison with the soils from the lake catchments. The depths corresponding to 1940 are 1.2, 3.2, 3.7 and 5.5 cm in Redon, Dlugi Staw, Starolesnianske Pleso and Ladove Lakes, respectively.

3.5. Vertical profiles in soils and sediments

In Figs. 3 and 4 the downcore profiles of the OC concentrations in the sediments and soils of Lakes Redon and Ladove are shown in the same graphs. The plots are only performed for comparison of the vertical structure of OC in soils and sediments. They do not involve temporal correspondences between the same depth levels.

The downcore OC profiles in the soils of both lakes generally exhibit higher abundances in the top sections (Figs. 3 and 4). This trend points to recent pollution episodes as the main factor for the occurrence of these compounds in these high mountains and is consistent with the observations in the sediments. However, both in Redon and Ladove the soil vertical profiles exhibit higher downcore spread than in the sediments (Figs. 3 and 4). This difference is observed in cases of both high and low OC soil pollution. Thus, DDTs, HCH and HCB in Redon Lake soils encompass the upper 4 cm whereas they only involve the upper 1 cm in the sediments. Similarly, at low OC concentration, e.g. PCB congeners #153, 138 and 180, there is a strong contrast between the concentration maxima found at the upper sections of the sediments and the maxima found at mid depths in the soil cores (Fig. 3). This difference suggests higher bioturbation in soils than sediments likely involving higher vertical OC spread in the former.

Further insight into the post-depositional changes in sediments and soil cores can be obtained by representation of the composition of the seven major PCB congeners, #28 + 31, 52, 90 + 101, 118, 153, 138 and 180, in both soil and sediments cores from all the lakes (Figs. 5 and 6). The upper sections are dominated by the heavier molecular weight congeners which are also the compounds found in higher concentration in the whole core. The incorporation of these compounds to both soil and lake sediments could be a consequence of their preferential condensation at the lake air temperatures (Grimalt et al., 2001; Simcik et al., 1999; Hippelein and McLachlan, 2000). The presence of these compounds in the air particulate phase may also enhance their preferential deposition although the condensation mechanism must dominate since these compounds are essentially found in the gas phase (van Drooge et al., 2002).

The concurrence of similar changes in downcore PCB congener predominance in both lake systems makes unlikely that these could reflect preferential deposition of congener mixtures dominated by the less chlorinated congeners in the past. In addition, there is not obvious reason for different deposition mechanisms in previous time periods. The dominance of the lower molecular weight PCB congeners at deeper sections is observed both in sediments and soils of both lakes being more significant in the later. Previous studies have already reported the occurrence of the less chlorinated PCB

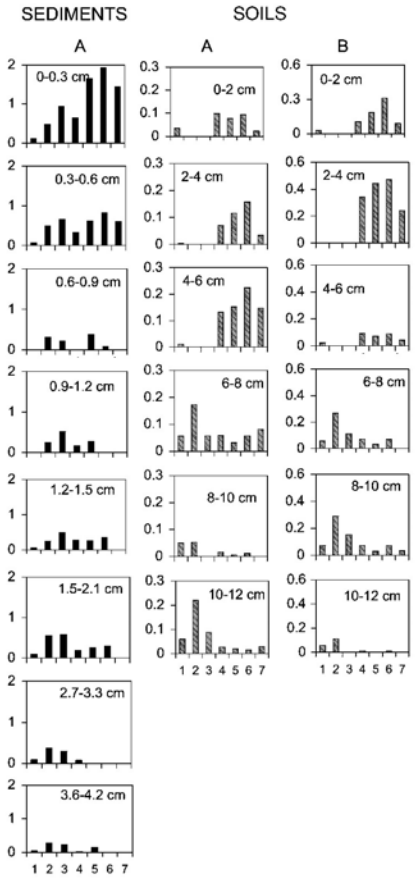

Fig. 5. Histograms showing the downcore composition of the major PCB congeners of the soils and sediment cores from Lake Redon. Foot captions as follows: (1) #28 + 31; (2) #52; (3) #90 + 101; (4) #118; (5) #153; (6) #138 and (7) #180. The plots compare vertical soil and sediment OC structures as indicated in Fig. 2.

congeners in deep soil sections corresponding to ages prior to commercial use (Sanders et al., 1995; Gevao et al., 1998) being attributed to vertical transport associated to water table oscillations or other physicochemical processes.

The increase in concentration with depth of the PCB congeners with lower degree of chlorination, e.g. #28 + 31 and 52 (Figs. 3 and 4), cannot be explained in terms of recent pollution inputs since the maxima are not close to the core tops. Two processes may explain the vertical distributions of these compounds. One concerns chemical diffusion, rainfall dissolution and water table oscillations (Rapaport and Eisenreich, 1988)

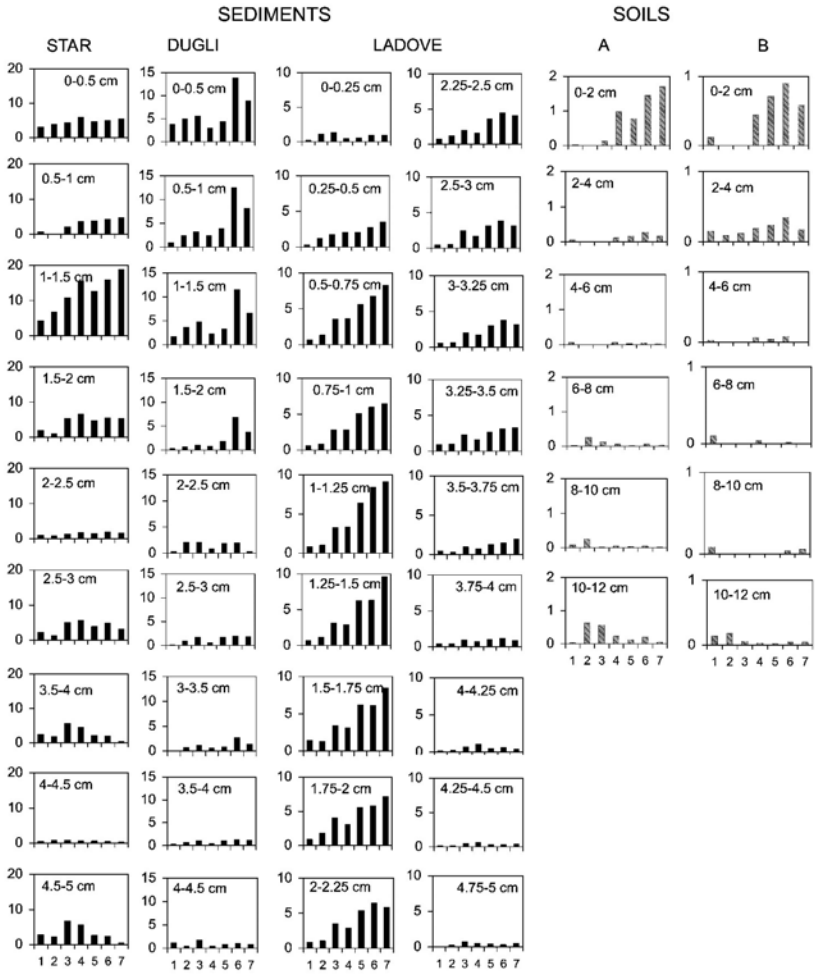

Fig. 6. Histograms showing the downcore composition of the major PCB congeners of the soils and sediment cores taken in the Tatra Lakes. Foot captions as in Fig. 5. The plots compare vertical soil and sediment OC structures as indicated in Fig. 2.

enhancing the vertical transport of the more water soluble less chlorinated PCB. Alternatively, the higher abundance of the less chlorinated congeners may reflect downcore in situ production. The fact that these downcore concentration peaks are only observed for the less chlorinated PCB congeners points to dechlorination as a likely mechanism for their formation (Quensen et al., 1988). Simple examination of the composition of some of the major PCB congeners present in these soils and sediments, e.g. #101, 118, 138, 153 and 180, show that they could be transformed into congeners #52 and 28 upon dechlorination. This process usually requires anaerobic conditions which may be encountered in microsites, in flooded or poorly drained soils (Haluska et al., 1995).

4. Conclusions

The concentrations of HCB, HCH, DDTs and PCBs in the soils and sediments from the lakes in the Pyrenees and the Tatra mountains exhibit parallel geographic distributions involving similar atmospheric mechanisms for the transport of these compounds to these two high-altitude sites. In general, DDTs were the most abundant OC, followed by total PCBs and HCB. In any case, the

concentrations of all OC are low suggesting absence of major pollution sources in these high mountain regions.

The vertical profiles of all OC from both soils and sediments exhibit higher abundances in the top sections, which indicate recent pollution episodes as the main reason for the occurrence of these compounds in the high mountain cores. However, both in Redon and Ladove Lakes the vertical profiles exhibit higher concentration gradients in the top sections of the sediments than in the soils which could reflect higher bioturbation in the later. In addition, the average OC concentrations are higher in sediments than soils in all cases. Both features point to higher retention efficiency of these compounds in the lake systems than in the catchment. In this respect, radiometric analysis shows that catchment to lake erosive transport of soil residues is minimal.

The higher sediment retention affinity does not reflect organic matter differences between soils and sediments since in most cases the former exhibit larger TOC than the latter. The constant low temperatures at the lake bottom (about 4 °C in all seasons) may be an important factor for the retention of these compounds. In contrast, soil temperatures have a strong seasonal variability reaching values higher than 10 °C in the warm periods. These higher temperatures may enhance soil bioturbation in the warm periods and increase volatilization back to the atmosphere after deposition.

The qualitative PCB distributions of soil cores are dominated by high molecular weight congeners in the top core sections and by the less chlorinated congeners at the bottom. Anaerobic microbial processes are currently invoked for the dechlorination of higher molecular weight congeners in soil/sedimentary environments. In the soils under study, these processes could occur in microsites, e.g. as observed in flooded or poorly drained soils. They also could be concurrent with bioturbation.

Acknowledgements

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Article 8.

POLYCYCLIC AROMATIC HYDROCARBON COMPOSITION IN SOILS AND SEDIMENTS OF HIGH ALTITUDE LAKES

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Polycyclic aromatic hydrocarbon composition in soils and sediments of high altitude lakes

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Abstract

The polycyclic aromatic hydrocarbons (PAH) in lake sediments and nearby soils of two European high mountain regions, Pyrenees and Tatra, have been studied. Similar mixtures of parent PAH were predominant in all cases, indicating a predominance of airborne transported combustion products. PAH in superficial layers of soils exhibited a better parallelism with PAH in long-range transported aerosol mixtures than in sediments. This higher agreement is observed when comparing the composition of both photochemically refractory and labile compounds. The contrast between these two environmental compartments points to significant PAH degradation during lake water column transport.

Postdepositional transformation processes were different in soils than in sediments. In the former there is higher decomposition of more labile PAH such as benz[*a*]anthracene, benzo[a]pyrene and methylphenanthrenes in relation to chrysene+triphenylene, benzo[e]pyrene and phenanthrene, respectively, which involves better long-term post-depositional preservation conditions in lake sediments.

In addition, the deep lake sediments involve the in situ diagenetic formation of major amounts of perylene, which is not formed in soil cores. In contrast, soils exhibit downcore enrichments of phenanthrene maybe as consequence of the extensive aromatization of diterpenoids. Evaluation of the downcore profiles of retene in comparison to those of benzo(*b*)naphtho[2,1-*d*]thiophene), 1,7- and 2,6-dimethylphenanthrene also suggests a diagenetic origin for this diterpenoid in the lake sediments.

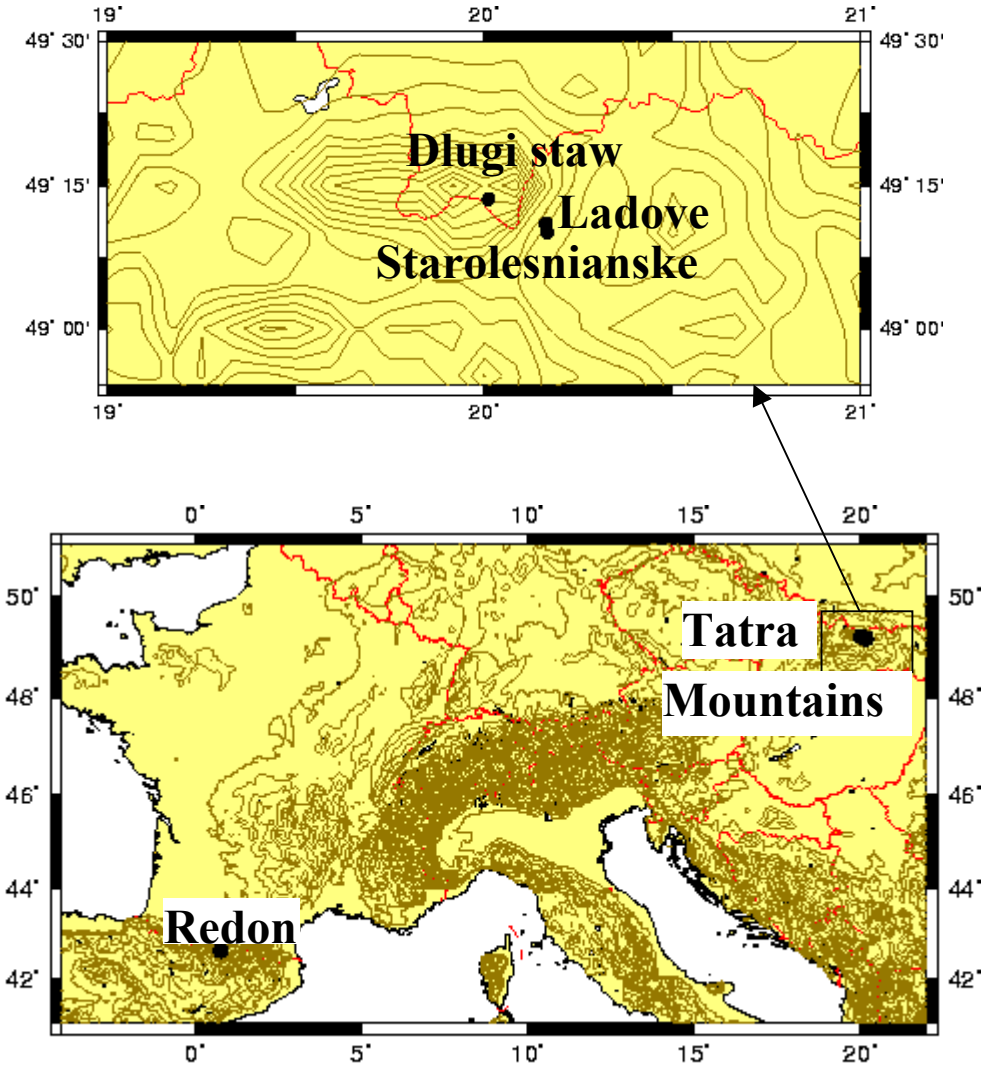

Fig. 1. Map showing the location of the soils and sediments sampled in high mountain European regions. Pyrenees, Redon (soils and sediments). Tatra, Ladove (soils and sediments), Dlugi staw and Starolesnianske pleso (sediments).

1. Introduction

PAH in the environment are deserving increasing attention for their widespread occurrence and mutagenic, carcinogenic and teratogenic effects (Freitag et al., 1985). They may be generated from organic matter diagenesis and anthropogenic processes (Simoneit, 1977; LaFlamme and Hites, 1978; Wakeham et al., 1980a and b). However, the anthropogenic contribution usually outweighs the inputs from other sources and is responsible for their general increase over the last 100 yr (Hites et al., 1977, Fernández et al., 2000).

Depending on their physico-chemical properties, atmospheric PAH are distributed between the gas and particulate phases, mainly in association with small particles (< 1 um) (Aceves and Grimalt, 1993; Masclet et al., 1988; Allen et al., 1996; Ribes et al., 2003). They are transported through the atmosphere to remote sites giving rise to a general background level in soils (Hartmann, 1996; Wilcke and Zech, 1997; Wild and Jones, 1995; Vogt et al., 1987; Berteigne et al., 1988; Jones et al., 1989a and b; Guggenberg et al., 1996; Wilcke et al., 1996) and lake sediments (LaFlamme and Hites, 1978; Gschwend and Hites, 1981; Atlas et al., 1981; Simcik et al., 1996; Fernández et al., 1996; 1999; 2000) where they accumulate due to their high stability and small mobility as consequence of their low water solubility. Soils and lake sediments are therefore good environmental compartments to record the historical environmental burden of these compounds as consequence of human activities.

In this respect, European high mountain lakes have been observed to accumulate significant loads of atmospherically transported PAH despite of their remoteness (Fernández et al., 1996; 1999; 2000; Carrera et al., 2001; Vilanova et al., 2001). These lakes are defined as those situated above the local tree-line, far from any pollution source and lacking major water inputs from the catchment. They constitute unique environments for the assessment of the atmospheric pollution load over continental areas. Geographical and historical patterns of this pollution load in Western Europe have been described recently based on the study of sediments from these lakes (Fernández et al., 1999; 2000). However, PAH not only accumulate in lake sediments but also in other environmental compartments such as soils. A global understanding of their overall burden in these high mountain areas also requires the study of this compartment.

High mountain areas are therefore ideal environments for comparison of PAH accumulation in soils and lake sediments since both compartments are under the same atmospheric precipitation fluxes. Accordingly, the Pyrenees and the Tatra mountains have been selected for the study of PAH in lake sediments and nearby soils.

The Pyrenees are a mountain range where moderate pollution levels by PAH have been recorded (Fernández et al. 1999; 2000). Lake Redon (42º38'34"N, 0º46'13"E; 2240 m above sea level; Fig. 1) is the largest high mountain lake in this area (24 ha) and has been used as reference lake for many environmental studies. Two lake sediment cores and two soil cores collected nearby

the lake are considered in the present study. The sediment cores, A and B, were retrieved from the deeper parts of the two basins, 73 and 32 m water column depth, respectively.

The Tatra mountains are situated in central Europe and constitute one of the most polluted mountain range for these compounds (Fernández et al. 1999; 2000). Two soil and one sediment cores from Ladove Lake (49º11'03"N, 20º09'46"E; 2057 m) were collected. The sediment core is compared to others collected in lakes from the same mountain range such as Starolesnianske Pleso (49°10'48"N, 20°10'4"E; 2000 m) and Dlugi Staw (49º13'36"N, 20º0'39"E; 1783 m) (Fig. 1). Lakes Ladove and Starolesnianske Pleso are situated less than 2 km apart.

To the best of our knowledge, this is the first study comparing the distribution of PAH in soils and lake sediments, particularly in high mountain areas.

2. Materials and Methods

2.1. Materials

Residue analysis *n*-hexane, dichloromethane, iso-octane, methanol and acetone were from Merck (Darmstadt, Germany). Anhydrous sodium sulfate for analysis was also from Merck. Neutral aluminum oxide type 507C was from Fluka AG (Buchs, Switzerland). Cellulose extraction cartridges were from Whatman Ltd (Maidstone, England). Aluminum foil was rinsed with acetone and let dry at ambient temperature prior to use. The purity of the solvents was checked by gas chromatography-mass spectrometry (GC-MS). No significant peaks should be detected for acceptance. Aluminum oxide, sodium sulfate and cellulose cartridges were cleaned by Soxhlet extraction with hexane:dichloromethane (4:1, v/v) during 24 h before use. The purity of the cleaned reagents was checked by ultrasonic extraction with *n*-hexane:dichloromethane (4:1; 3 x 20 mL), concentration to 50 μL and analysis by GC-MS. No interferences were detected. Sodium sulfate and aluminum oxide were activated overnight at 400ºC and 120ºC, respectively.

2.2. Sampling

Sediment samples were taken in the deepest points of the lakes using a gravity coring system (Glew, 7.5 cm diameter, 30 cm long). A 7 cm (diameter) x 20 cm (long) stainless steel cylinder was used for soil core collection. All soils were taken within the lake catchment areas. The sediment samples except those from Ladove Lake were collected between 1993 and 1994 whereas the soil cores and the sediments from Ladove Lake were sampled in 2001. Immediately after sampling soil and sediment cores were divided in sections of 2 and 0.5 cm, respectively (0.3 and 0.25 cm in the case of Redon and Ladove sediments, respectively), and stored in pre-cleaned aluminium foil at –20°C until analysis.

2.3. Analysis

The following PAHs were determined in both soils and sediments: acenaphtene, acenaphtylene, fluorene, phenanthrene, anthracene, dibenzothiophene, methylphenanthrenes (3-MPhe, 2-MPhe, 9+4-MPhe, 1-MPhe), methyldibenzothiophenes (4-MDBT, 3+2-MDBT, 1-MDBT), fluoranthene, pyrene, dimethylphenanthrenes (3,6-DMPhe, 2,6-DMPhe, 2,7-DMPhe, 1,3+2,10+3,9+3,10-DMPhe, 1,6+2,9-DMPhe, 1,7-DMPhe, 2,3-DMPhe, 1,9+4,9-DMPhe,1,8-DMPhe), retene, benzo(*b*)naphtho[2,1-*d*]thiophene, benz[*a*]anthracene, chrysene+triphenylene (they coeluted upon GC-MS analysis so they were considered together), benzo[*b*+*j*]fluoranthenes, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, dibenz[*a,h*]anthracene and coronene.

2.4. Sample extraction

Soils (25-50 g) were weighed into a Whatman Soxhlet cellulose thimble. About 1:1 w/w sodium sulfate were mixed with the soil in order to improve Soxhlet extraction by water removal. Samples were extracted with hexane:dichloromethane (4:1) for 18 h. Standards of d_{10}-anthracene, d_{10}-pyrene, d_{12}-benz[*a*]anthracene and d_{12}-benzo[*ghi*]perylene were added to the extracts that were first concentrated by rotary vacuum evaporation to 3-5 mL and subsequently eluted through a drying column filled with 1 g of anhydrous sodium sulfate.

After rotary vacuum evaporation to ~0.5 mL, the extracts were fractionated on a neutral aluminum oxide column (2 g). A first non-polar fraction was obtained by elution with 8 mL of hexane:dichloromethane (9:1). The second, obtained by elution with 10 mL of hexane:dichloromethane (1:2), corresponded to the fraction of PAHs and other aliphatic esters. This PAH fraction was then hydrolyzed overnight with KOH in methanol for removal of the aliphatic esters. Neutral compounds were recovered with *n*-hexane and fractionated again by adsorption chromatography with aluminum oxide (2 g). After elution with hexane:dichloromethane (1:2), the PAH fraction was concentrated to 50μL in isooctane by rotary vacuum evaporation followed by a gentle stream of purified N_2.

For sediments, about 0.1-1 g of wet sediment was extracted by sonication with methanol (1 x 20 mL; 20 min) in order to separate most of the interstitial water from the sediment. The subsequent extractions were performed with (2:1, v/v) dichloromethane-methanol (3x20 mL; 20 min). All extracts were combined and spiked with deuterated PAH internal standards (d_{10}-anthracene, d_{10}-pyrene, d_{12}-benz[*a*]anthracene and d_{12}-benzo[*ghi*]perylene). Then, they were vacuum evaporated to almost 10 mL and hydrolyzed overnight with 20 mL of 6% (w/w) KOH in methanol. The neutral fractions were recovered with n-hexane (3 x 10 mL), vacuum evaporated to almost dryness, and fractionated with a column containing 2 g of alumina. The aromatic fractions (10 mL of dichloromethane: *n*-hexane, 2:1) were vacuum and nitrogen concentrated almost to dryness and redissolved in isooctane prior to GC-MS analysis.

2.5. Instrumental analysis

The internal standard d_{12}-perylene (L.D. Ehrenstorfer) was added to the vials prior to injection. Samples were injected into GC-MS (Fisons 8000 Series, Mass Selective Detector 800 Series). A fused silica capillary column, HP-5 of 50 m and 0.25 mm i.d (0.25 μm film thickness) was used. The oven temperature program started at 90°C (1 minute hold), followed by a 4°/min ramp up to 300°C (15 minutes hold). Injector, transfer line and ion source temperatures were 280°C, 300ºC and 200°C, respectively. Helium was used as carrier gas (1.1 mL/min). PAH were determined in the electron impact and selected ion recording modes. The following mass fragments were used for identification and quantification: m/z 166, 178, 184, 192, 202, 206, 219, 226, 228, 234, 252, 276, 278, and 300 (dwell time 40 ms per single ion, ion window according to retention times of standards). Diagnostic ions of the corresponding perdeuterated standards m/z : 188, 212, 240, 264, and 288 were also used.

2.6. Quantification

Quantification was performed by combination of the external standard (EPA, Mix 9 Dr Ehrenstorfer) and retention index methods. Calibration curves (detector response *vs* amount injected) were performed for each compound. The range of linearity of the detector was evaluated from the curves generated by representation of detector signal/amount injected *vs* amount injected. All measurements were performed in the ranges of linearity found for each compound. The quantitative data were corrected for surrogate recoveries.

2.7. Quality control

Procedural blanks were performed with each set of 9 samples to check for the presence of interfering peaks. Recoveries of d_{10}-anthracene, d_{10}-pyrene, d_{12}-benz[*a*]anthracene and d_{12}-benzo[*ghi*]perylene averaged 60, 70, 76 and 82%, respectively. Replicate analysis of soil samples gave an error $<\pm 15$ %. The method detection limits based on signal to noise ratio of 3 in real samples ranged from 100 (compound) to 400 pg (compound). Both soil and sediment analytical procedures were successfully calibrated with a standard reference material with certified PAH values (marine sediment HS-4, Institute for Marine Biosciences, Canadian National Research Council).

2.8. Total Organic Carbon

Soil and sediment samples were treated with HCl 3N to remove inorganic carbon. Subsequently, they were cleaned with Milli-Q water until neutral pH (7 ± 0.2) and dried at 60ºC. The determination of TOC was performed by flash combustion at 1025°C followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. The limit of detection was 0.1 %.

2.8. Radiometric dating

Sediment and soil samples were analysed for ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am by direct gamma assay using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors (Appleby et al. 1986). ^{210}Pb was determined via its gamma emissions at 46.5 keV and ^{226}Ra by the 295 keV and 352 keV γ-rays emitted by its daughter isotope ^{214}Pb following 3 weeks storage in sealed containers to allow radioactive equilibration. ^{137}Cs and ^{241}Am were measured by their emissions at 662 keV and 59.5 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Corrections were made for the effect of self absorption of low energy γ-rays within the sample (Appleby et al. 1992). Supported ^{210}Pb activity was assumed to be equal to the measured ^{226}Ra activity. Unsupported ^{210}Pb activity was calculated by subtracting supported ^{210}Pb from the measured total ^{210}Pb activity. ^{210}Pb radiometric dates were calculated using the CRS and CIC dating models (Appleby and Oldfield, 1978) where appropriate and validated where possible against the 1986 and 1963 depths determined from the ^{137}Cs/^{241}Am stratigraphic records.

Table 1. Average PAH concentrations, PAH ratios and TOC in the soil and sediment cores from Lake Redon.

	0-2 cm	2-4 cm	4-6cm	6-8 cm	8-10 cm	10-12 cm
		SOILS				
Parent PAH[a]	770	670	190	34	39	47
Fla/(Pyr+Fla)	0.61	0.58	0.54	0.54	0.57	0.56
BaA/(BaA+C+T)	0.21	0.24	0.24	0.17	0.11	0.19
BaP/(BaP+BeP)	0.32	0.35	0.39	0.37	0.34	0.43
Ind/(Ind+Bghi)	0.55	0.57	0.56	0.56	0.55	0.56
SUM MPhe/(SUM MPhe+Phe)	0.45	0.56	0.59	0.28	0.46	0.48
Ret/(Ret+BNT)	0.32	0.01	0.45	0.89	0.58	0.35
1,7-/(1,7- + 2,6-)DMPhe	0.70	0.67	0.62	0.77	0.67	0.62
TOC (g/g dw)	0.33	0.30	0.23	0.18	0.16	0.21
		SEDIMENTS[b]				
Parent PAH[a]	760	550	100	130	87	
Fla/(Pyr+Fla)	0.65	0.68	0.59	0.57	0.67	
BaA/(BaA+C+T)	0.16	0.13	0.12	0.12	0.12	
BaP/(BaP+BeP)	0.20	0.20	0.25	-[c]	-	
Ind/(Ind+Bghi)	0.62	0.63	0.64	0.78	0.69	
SUM MPhe/(SUM MPhe+Phe)	0.33	0.58	0.47	0.44	0.20	
Ret/(Ret+BNT)	0.21	0.28	0.85	-	0.74	
1,7-/(1,7- + 2,6-)DMPhe	0.56	0.62	0.63	0.49	0.67	
TOC (g/g dw)	0.04	0.04	0.05	0.04	0.04	

[a]Units in ng/g dry weight. These values correspond to the sum of all compounds indicated in the caption of Figure 2 except perylene. [b]Core B. [c]Not determined because of interferences from the huge amount of perylene.

Table 2. Average PAH concentrations, PAH ratios and TOC in the soil and sediment cores from Ladove lake.

Core Sections:	0-2 cm	2-4 cm	4-6cm	6-8 cm	8-10 cm	10-12 cm
SOILS						
Parent PAH[a]	1900	3400	430	75	63	90
Fla/(Pyr+Fla)	0.71	0.54	0.57	0.61	0.52	0.50
BaA/(BaA+C+T)	0.32	0.23	0.14	0.13	0.11	0.13
BaP/(BaP+BeP)	0.42	0.39	0.27	0.18	0.31	0.26
Ind/(Ind+Bghi)	0.53	0.47	0.39	0.30	0.47	0.46
SUM MPhe/(SUM MPhe+Phe)	0.34	0.37	0.78	0.48	0.18	0.25
Ret/(Ret+BNT)	0.29	0.02	0.02	0.05	0.14	0.04
1,7- /(1,7- + 2,6-)DMPhe	0.79	0.63	0.77	0.79	0.56	0.59
TOC (g/g dw)	0.23	0.16	0.12	0.07	0.07	0.07
SEDIMENTS						
Parent PAH[a]	12000	11000	3000	3000		
Fla/(Pyr+Fla)	0.62	0.61	0.60	0.59		
BaA/(BaA+C+T)	0.18	0.18	0.17	0.19		
BaP/(BaP+BeP)	0.30	0.28	0.29	0.30		
Ind/(Ind+Bghi)	0.56	0.56	0.54	0.53		
SUM MPhe/(SUM MPhe+Phe)	0.26	0.25	0.27	0.25		
Ret/(Ret+BNT)	0.03	0.06	0.14	0.22		
1,7-/(1,7- + 2,6-)DMPhe	0.61	0.62	0.68	0.79		
TOC (g/g dw)	0.08	0.07	0.07	0.07		

[a]Units in ng/g dry weight. These values correspond to the sum of all compounds indicated in the caption of Figure 2 except perylene.

3. Results and Discussion

3.1. Lake features

The lakes considered in this study are situated above the local tree line, they are oligotrophic (median total phosphorous 4.1 μg/L) and remain ice-covered for long periods. Three dominant types of land cover are found in the lake catchments, dry alpine meadows, moraines and solid rock. Among these, the former were selected for study. Soils in the dry alpine meadows are mostly undeveloped (e.g. leptosol, podsol and histosol) with average mineral horizons of about 33 cm thickness and shallow organic matter horizons (5-17 cm, average 4 cm). These soils are covered by grass in summer and under snow during the cold months (Catalan, 1988). Pollution inputs are related to atmospheric transport since the lakes are free from local anthropogenic sources. Nevertheless, significant differences in pollution load are observed in both lake groups since much higher PAH levels are encountered in Tatra mountains (Fernández et al. 1999; 2000).

TOC exhibits much higher values in the soils than in the sediments of Lake Redon, 16-33% and 4-5%, respectively (Table 1). In Ladove lake, higher TOC values are also found in soils than sediments in the upper 6 cm, 12-23% and 7-8.3%, respectively (Table 2). However, between 6-8 cm the difference between the two environmental compartments vanishes, 7% in both cases (Table 2). A strong depth-dependent TOC decrease is therefore observed in Ladove soils whereas sedimentary TOC remains nearly constant. In Lake Redon, soil TOC values also decrease significantly with depth, from 33% to 16-21%, whereas the sediment values are nearly constant (Table 1).

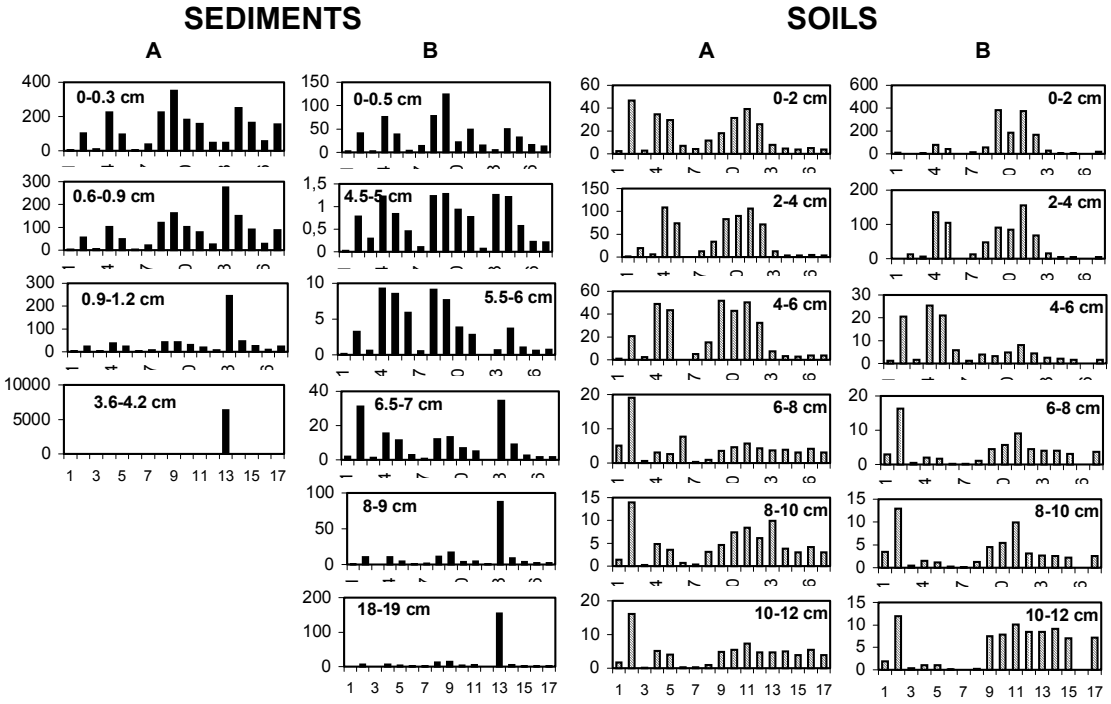

Fig. 2. PAH in the soils and sediments from Lake Redon. A and B refer to different cores analysed in the lake surroundings. 1, fluorene; 2, phenanthrene; 3, anthracene; 4, fluoranthene; 5, pyrene; 6, retene; 7, benz[*a*]anthracene; 8, chrysene+triphenylene; 9, benzo[*b*+*j*]fluoranthenes; 10, benzo[*k*]fluoranthene; 11, benzo[*e*]pyrene; 12, benzo[*a*]pyrene; 13, perylene; 14, indeno[1,2,3-*cd*]pyrene; 15, benzo[*ghi*]perylene; 16, dibenz[*a,h*]anthracene, 17, coronene. PAH units in ng/g.

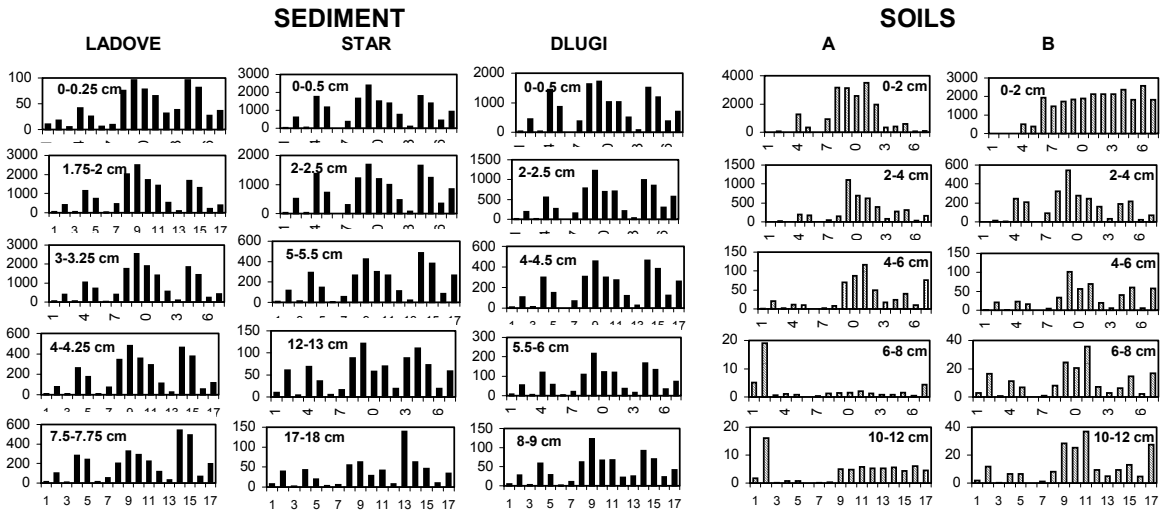

Fig. 3. PAH in the soils and sediments from Ladove lake. Numbers in abscissas as in Fig. 2. PAH units in ng/g.

3.2. PAH distributions

The PAH distributions found in the sediments and soils of the Pyrenees and Tatra lakes are shown in Figs. 2 and 3. The distributions are always dominated by parent PAH, from phenanthrene to coronene, with a predominance of high molecular weight compounds of catacondensed structures in the upper sections. Total methylated + dimethylated PAH were in low amounts (0.2-10% of total PAH).

The PAH distributions in the sediments from Pyrenees and Tatra mountains are remarkably similar despite the variability of PAH sources to the atmosphere. This similarity is also observed independently of the high differences in PAH load between the Pyrenees and Tatra which, in terms of sedimentary concentration, involve top sediment concentrations of 980 and 12000 ng/g total PAH, respectively (Tables 1 and 2). This uniform sedimentary PAH profile exhibits a high parallelism with the PAH composition in the atmospheric aerosols collected at these high altitude sites (Fernández et al., 2002). This PAH distribution is quite ubiquitous and has been reported in sediments from remote/rural areas (Sanders et al., 1993; Tolosa et al., 1996; Fernández et al., 1999; 2000) and corresponds to the airborne combustion mixtures refractory to photooxidation and chemical degradation (Simcik et al., 1996; Simó et al., 1997).

The soil PAH mixtures also exhibit a predominance of parent PAH in which the heavier molecular weight compounds are present in higher relative proportion (Figs. 2 and 3). However, the qualitative and quantitative differences between soil cores from the same area are higher. Thus, the top distributions in the Tatra lakes exhibit high relative concentrations of chrysene+triphenylene, benzo[*b+j*]fluoranthenes, benzo[*k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene in both cores. Nevertheless, one of them, B (Fig. 3), also has benz[*a*]anthracene, perylene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, dibenz[*ah*]anthracene and coronene in high relative proportion. These compounds are not so significant in core A (Fig. 3). The PAH top soil distributions of Lake Redon are also dominated by benzo[b+*j*]fluoranthenes, benzo[*k*]fluoranthene, benzo[*e*]pyrene and benzo[*a*]pyrene but in one case, A (Fig. 2), phenanthrene, fluoranthene and pyrene are also present in significant relative concentration.

3.3. Regular differences in soil and sediment PAH composition

The PAH ratios of some soil and sediment sections from Redon and Ladove lakes are compared in Tables 1 and 2. The ratios are grouped in core sections only for comparison of the vertical PAH structure. The grouping does not involve temporal correspondences between the same soil and sediment depth levels.

The benz[*a*]anthracene/(benz[*a*]anthracene + chrysene+triphenylene) ratios from the upper core sections exhibit higher values in the soils than in the sediments. Thus, in Lake Redon (0-8 cm) the differences range between 0.17-0.24 in the former case and between 0.12-0.15 in the second (Table 1). In Ladove lake (0-4 cm) the values span between 0.23-0.32 in soils and exhibit a constant ratio of 0.18 in the sediments (Table 2). However, in the deeper sections the ratios of the

soil values are lower, e.g. 0.11 and 0.12 for soils and sediments of Lake Redon (8-10 cm), respectively (Table 1), and 0.13-0.14 and 0.17-0.19 for the soils and sediments of Ladove lake (4-8 cm), respectively (Table 2).

Benz[*a*]anthracene is more labile to photo-oxidation than chrysene+triphenylene (Kamens et al., 1986; 1988). Accordinlgy, the benz[*a*]anthracene/(benz[*a*]anthracene + chrysene+triphenylene) ratio in atmospheric aerosols collected over high mountain lakes has average values of 0.12 in summer and 0.35 in winter (Fernández et al., 2002). Having in mind that PAH are present in higher concentration in the winter samples (Fernández et al., 2002), the soil ratios in the top sections of the soil cores are likely more representative of the PAH atmospheric fallout. Benz[*a*]anthracene is also less stable than chrysene+triphenylene upon diagenesis since the highest relative content in the former is generally encountered in the top core layers. The difference between soils and sediments suggests that the original atmospherically-transported PAH composition is initially better preserved in the soils (upper core sections) but at deeper core sections the benz[*a*]anthracene/(benz[*a*]anthracene + chrysene+triphenylene) ratio deviates further from the original mixtures in soils than sediments.

Benzo[*a*]pyrene is photochemically less stable than benzo[*e*]pyrene (Nielsen 1988). In the top cores (0-4 cm) the benzo[*a*]pyrene/(benzo[*a*]pyrene + benzo[*e*]pyrene) ratios show higher values in the soils than in the sediments. Thus, in Lake Redon they range between 0.32-0.35 and 0.22-0.23, respectively (Table 1), and in the Tatra lakes between 0.39-0.42 and 0.28-0.30, respectively (Table 2).

The benzo[*a*]pyrene/(benzo[*a*]pyrene + benzo[*e*]pyrene) ratios in aerosols collected in high mountain regions average 0.27 in summer and 0.41 in winter (Fernández et al., 2002). Again, considering the higher PAH load in winter than in summer the soil values are more likely to reflect better the original PAH atmospheric composition. At deeper core sections no significant change is observed in the sediments, e.g. 0.25 and 0.29-0.30 in Redon and Ladove, respectively. Similarly, the deeper soil sections of Lake Redon exhibit ratios between 0.34 and 0.43 (Table 1). However, in Ladove soils the deep section ratios show larger scatter and lower values (0.18-0.31; Table 2). In some deeper soil sections the benzo[*a*]pyrene/(benzo[*a*]pyrene + benzo[*e*]pyrene) ratios are even lower than those of sediments showing that benzo[*a*]pyrene is less preserved in the former than the latter.

The ratio between phenanthrene and its methyl derivatives is also labile to photooxidation, the transformation involving a loss of methylated compounds upon long-range transport (Simó et al., 1997). Comparison of the methylphenanthrenes/(methylphenanthrenes + phenanthrene) ratio in soils and sediments shows ranges between 0.28-0.59 and 0.20-0.47, respectively, in Lake Redon (Table 1), and between 0.18-0.78 and 0.25-0.30, respectively, in Ladove lake (Table 2). In all cases except one section of Lake Redon (6-8 cm) the ratio is higher in the soil than in the sediments showing a better preservation of the more labile compounds in the former.

The indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[*ghi*]perylene) ratio is a priori more stable to photooxidation than the ratios discussed above. In Redon it ranges between 0.55-0.57 and 0.62-0.78 in soils and sediments, respectively (Table 1), and in Ladove lake between 0.30-0.53 and 0.53-0.56 in soils and sediments, respectively (Table 2). The measured range in high mountain aerosols is 0.55 in both winter and summer (Fernández et al., 2002). These values are again closer to the soil than to the sediment values in Lake Redon. In contrast, in Ladove lake there is a higher difference between the atmospheric ratio and those in soils than in sediments. There is no obvious explanation for this deviation although it must be indicated that the aerosol values taken as reference (Fernández et al., 2002) correspond to a series of data including atmospheric samples from Lake Redon but not from the Tatra mountains.

The fluoranthene/(fluoranthene + pyrene) ratios in soils range between 0.54-0.61 and 0.50-0.71 in Lakes Redon and Ladove. In the sediments they range between 0.59-0.66 and 0.59-0.62 at these two sites, respectively (Tables 1 and 2). The average values of this ratio in the high mountain aerosols are 0.44 in summer and 0.59 in winter (Fernández et al., 2002). The winter values are closer to those in the soils than in the sediments from Lake Redon but in Ladove lake the sediment values are the closest to this mountain aerosol winter ratio. In any case the differences between soils and sediments are small in the case of fluoranthene/(fluoranthene + pyrene) ratios.

3.4. Downcore sedimentary PAH

Radiometric analysis shows that all lake sediment cores selected for study have rather uniform sedimentation. No hiatus or periods of mixing were observed in the vertical structure of the recovered sediments. The average sedimentation rates of the sediment cores studied were 0.024, 0.054, 0.084 and 0.10 cm/y for Redon, Dlugi Staw, Starolesnianske Pleso and Ladove. These rate differences and the core sectioning for analysis provide vertical PAH profiles with different time resolutions at each site.

The best time resolved PAH trend is the one for Ladove Lake where biannual resolution is achieved in most core sections between 1924 and 2001 (Figure 4). Total pyrolytic PAH were maxima between 1980 and 1988. Another period of maximum PAH input was observed between 1963-1966. Before this time, 1924-1954, much lower PAH concentrations are observed. On the other hand, after the 1988 PAH maximum, a strong decrease in PAH concentrations is found which extends up to 2001 (the most recent recorded date in the sediment collected). This PAH decrease is consistent with the improvement of the combustion techniques in central Europe.

The pyrolytic PAH in the other lakes from the Tatra mountains exhibit similar profiles but with smaller temporal resolution. As these cores were taken in 1993, the most recent PAH decrease is not observed. Pyrolytic PAH in the sediment core of Lake Redon also exhibit a similar temporal trend. Like in the sediments from Dlugi Staw and Starolesnianske Pleso, the temporal resolution is lower than in Ladove lake and the most recent date recorded is 1994.

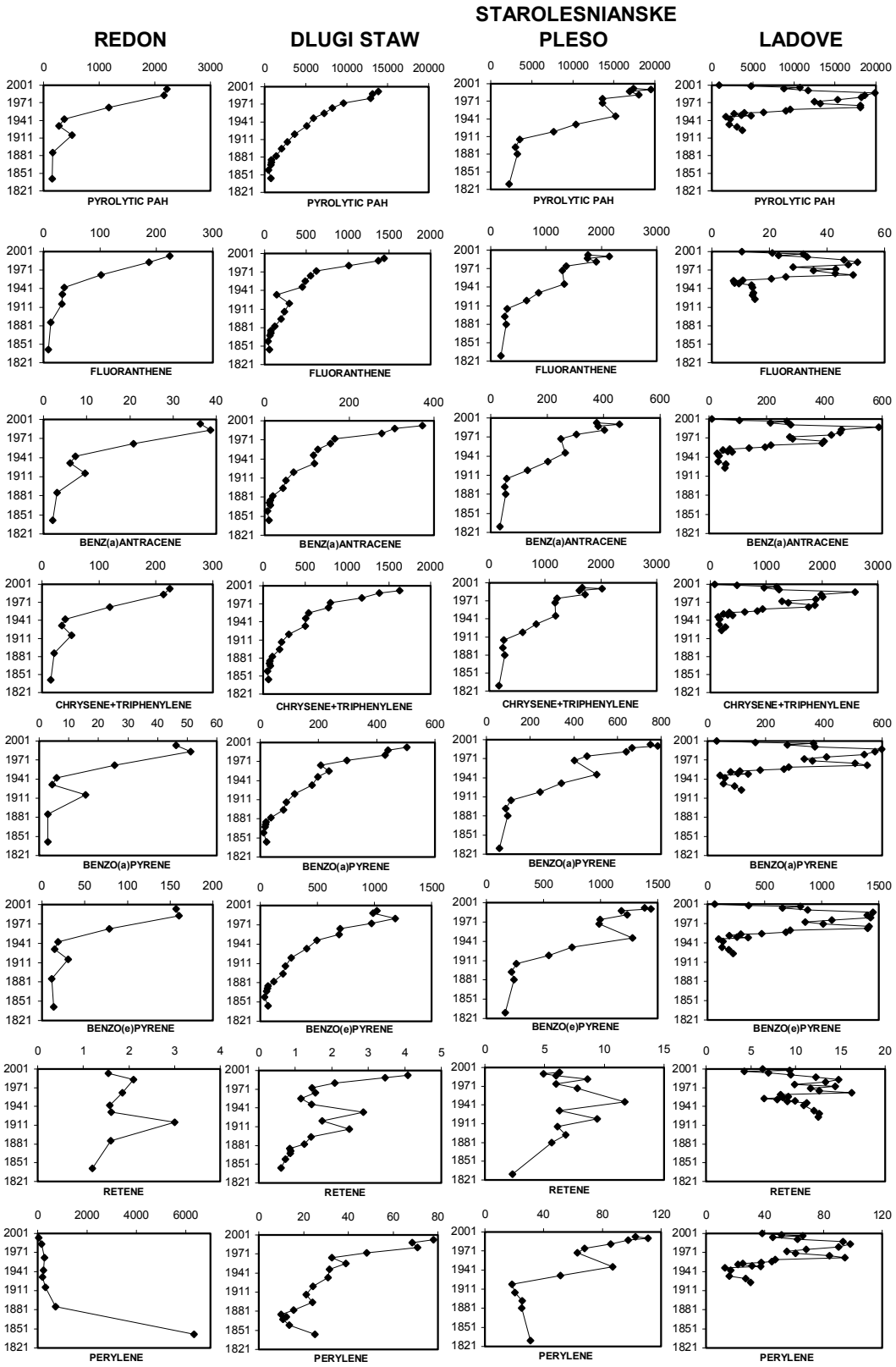

Fig. 4. Time scales of the concentrations of total pyrolytic PAH and selected parent PAH determined from the sediment cores analyzed in the Pyrenees and the Tatra mountains. PAH units in ng/g.

Representation of the temporal changes of the major parent PAH such as fluoranthene, benz[*a*]anthracene, chrysene+triphenylene, benzo[*a*]pyrene, benzo[*e*]pyrene and many others shows the same trends as for total pyrolytic PAH. Perylene is also showing the same temporal trend as the major pyrolytic PAH in the lakes from the Tatra mountains. However, in Lake Redon the highest values are observed at deep core sections. Thus, the downcore changes in PAH may reflect the atmospheric inputs of these compounds arriving to the high mountain areas through time or in situ diagenetic processes involving the formation of some PAH such as perylene in Lake Redon.

Retene is the compound exhibiting a more distinct behavior with time. Their downcore profiles do not show a steeper decrease since the concentrations in the ancient core sections are not too different from those in which highest total pyrolytic inputs are found.

3.5. Diagenetic formation of PAH

In Lake Redon, PAH qualitative distribution in the deeper sections show a high predominance of perylene, sections 0.9-4.2 cm in core A and 8-19 cm in core B (Fig. 2). This predominance also involves a net perylene concentration increase in both cores revealing in situ formation of this PAH, e.g. in the deeper sections of core A it reaches more than 6000 ng/g which is higher than all other PAH in all the other core sections (Fig. 2). In the Tatra mountains this trend is not observed (Figs. 3 and 4). Only in the deeper sections of Starolesniaske Pleso core a predominance of perylene is observed but without absolute concentration increase (Fig. 4).

The predominance of perylene in ancient sediment layers of freshwater (Wakeham et al., 1980a; Tan and Heit, 1981) and marine systems (Aizenshtat, 1973; Wakeham et al., 1979; Venkatesan, 1988) has been reported in the literature but its precursor/s still remain unknown. The downcore profiles observed in Lake Redon are consistent with an in situ production from sedimentary precursor/s which, considering the high dominance of terrigenous markers among the distributions of hydrocarbons and alcohols/sterols (data not reported here), are likely to be related to higher plant residues.

In contrast, no diagenetic formation of perylene is observed in the downcore soil PAH mixtures (Figs 2 and 3) where this hydrocarbon is always a minor component. Since most terrigenous inputs probably originate from the local grassland vegetation the difference from the sediment composition is probably related to the lack of anoxic conditions in the soils.

An enrichment in the relative concentration of phenanthrene is observed when considering the PAH downcore distributions in the soils (Figs. 2 and 3). However, this enrichment is only relative to the concentration of the other PAH. The increase in absolute concentration is small. A net production of phenanthrene after sedimentation is therefore unclear. This hydrocarbon is the end member product in the transformation of many diterpenoids following aromatization pathways (Simoneit, 1986; Simoneit et al., 1986).

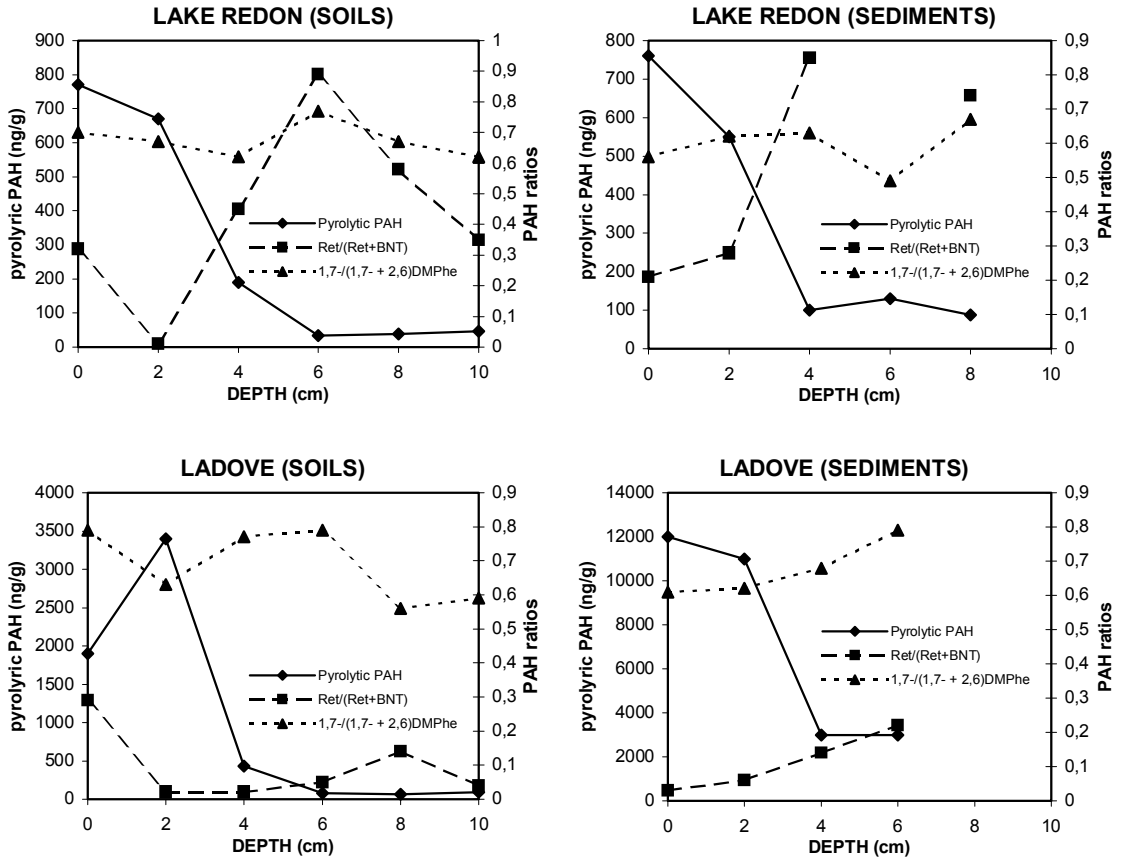

Fig. 5. Downcore distributions of pyrolytic PAH and the indices retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) and 1,7-dimethylphenanthrene/(1,7-dimethylphenanthrene + 2,6-dimethylphenanthrene) in the soils and sediments from Redon and Ladove lakes.

Retene may be produced during wood combustion (Ramdahl, 1983) or diagenesis (Simoneit, 1977; LaFlamme and Hites, 1978; Wakeham et al., 1980b). In contrast, benzo(*b*)naphtho[2,1-*d*]thiophene is a specific marker of coal combustion (Fernández et al., 1996). Compilation of the retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) ratio affords therefore a standardized index for comparison of the downcore variation of retene vs the major pyrolytic inputs (Fig. 5). This index may be compared to the changes in 1,7-dimethylphenanthrene vs 2,6-dimethylphenanthrene which has also been proposed as a marker of wood to fossil fuel combustion (Benner et al., 1995) as shown in studies on lake Mystic and Boston harbor (Gustaffson et al., 1997). This index has been calculated for the soils and sediments of the high mountain lakes considered for study and compared to the retene index and total PAH (Fig. 5).

The 1,7-dimethylphenanthrene/(1,7-dimethylphenanthrene + 2,6- dimethylphenanthrene) exhibits similar values and a rather constant downcore profile in both Redon and Tatra sediments and soils. In contrast, the retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) index increases downcore

in the sediments of both lakes (Fig. 5). This increase is also observed in Redon soils but not in the Tatra soils. The sedimentary downcore increase of the retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) index and the nearly constant ratio of the 1,7-dimethylphenanthrene/(1,7-dimethylphenanthrene + 2,6-dimethylphenanthrene) sediment suggest that the presence of retene in the deeper sediments is due to diagenetic processes. Thus, in these high mountain environments it cannot be taken as a wood combustion marker.

CONCLUSIONS

In high mountain areas there is a better parallelism between the PAH composition in long-range transported aerosol mixtures and top soil sections than in top lake sediment layers. This higher agreement is observed when comparing diagnostic ratios such as indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene + benzo[*ghi*]perylene) but also ratios involving photochemically labile compounds such as benz[*a*]anthracene/(benz[*a*]anthracene + chrysene+triphenylene), benzo[*a*]pyrene/(benzo[*a*]pyrene + benzo[*e*]pyrene) and methylphenanthrenes/ (methyl-phenanthrenes + phenanthrene). In all cases, labile PAH are found in higher relative concentration in soils and the corresponding ratios are closer to those found in the aerosols than in the lake sediments. The contrast between these two environmental compartments points to significant degradation of labile PAH during water column transport from atmosphere to underlying sediments in high mountain lakes.

In contrast, at deeper core sections, higher relative proportion is found of the more labile PAH in sediments than soils. This is observed for the relative content of benz[*a*]anthracene to chrysene + triphenylene, benzo[*a*]pyrene to benzo[*e*]pyrene) and methylphenanthrenes to phenanthrene. Thus, after sedimentation, preservation of the labile PAH is better in the lake sediments than in soils from the catchment.

The diagenetic processes in soils and sediments are also different, involving the formation of major amounts of perylene in the later but not in the former. In soils downcore enrichment of phenanthrene is observed maybe as consequence of the extensive aromatization of diterpenoid compounds. In this respect, examination of the retene/(retene + benzo(*b*)naphtho[2,1-*d*]thiophene) and the 1,7-dimethylphenanthrene/(1,7-dimethylphenanthrene + 2,6-dimethylphenanthrene) ratios in sediments and soils indicates a diagenetic origin for this diterpenoid.

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Article 9.

CONGENER SPECIFIC ASSESSMENT OF GLOBAL ATMOSPHERIC PCB POOL

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Congener specific assessment of the global atmospheric PCB pool

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Abstract

An attempt has made to establish a Global atmospheric inventory on PCBs, based on atmospheric field data from 1990 until 2000 of individual PCB congenrs. Different approached have been applied in order to obtain an overview on the possible advantages and disadvantages of these approaches on the model. On the Northern Hemisphere a negative latitudinal correlation is observed, which is in agreement with the pseudo-enthalpies for evaporation of the congeners. On the Southern Hemisphere, due to lack of sufficient data, this correlation is not observed. Moreover, new data from the Islands of Hawaii shows very low PCB concentrations in this part of the Pacific Ocean. Since it seems that remote sites on the Northern Hemisphere are under influence of potential source areas, the Northern Hemisphere is divided in a part of ´continental influence´ and one without this influence. Further more, a vertical gradient on PCB concentration was applied. The calculated Global inventories show in general 2-3 times higher PCB amounts on the Northern Hemisphere than on the Southern Hemisphere. The Global inventory for ∑PCB is 63 tonnes and 32 tonnes for the model without and with the vertical PCB gradient. Implication of OH radical concentrations and calculated reaction rates between PCB and OH give very high PCB sink, which is primarily caused by both high PCB and OH concentrations in the tropical zones. These sinks have to be compensated by very high PCB emission, which does not occur. Implication of calculated residence times shows PCB loss which are closer to the annual estimated emission.

1. Introduction

In the last decades persistent organic pollutants such as polychlorinated biphenyls (PCB) have been banned in most industrialised countries. Accordingly, PCB decreases in lake waters, soils, peat and sediments have been identified in potential source areas where PCBs were produced and used [*Gobas et al.*,1995; *Jeremiason et al.,* 1994; *Eisenreich et al.,* 1989; *Wong et al.,* 1995; *Rapaport and Eisenreich,* 1988; *Kjeller and Rappe,* 1995; *Sanders et al.,* 1995]. However, these compounds are still omnipresent and the observed decreases in remote areas have been small if any [*Baker and Eisenreich,* 1990; *Panshin and Hites,* 1994; *Hillery et al.,* 1997; *Hung et al.,* 2001].

Elucidation of the temporal concentration trends of these compounds at a planetary scale and, subsequently, anticipation of their future effects in remote ecosystems requires an improved understanding of the processes controlling their losses in the environment. Volatilization is responsible for a significant proportion of PCB decline in the source areas, involving a net flux of compounds from soils and waters to the atmosphere [*Jeremiason et al.,* 1994; *Alcock et al.,* 1993]. In this sense, PCBs are possibly not eliminated from the environment but merely translocated by atmospheric transport to other areas. This atmospheric compartment is the most important medium for the long range distribution of PCBs, including transport to the marine system, the arctic and high mountain areas [*Duce et al.,* 1991; *Ballschmiter,* 1992; *Iwata et al.,* 1993; *Tolosa et al.,* 1997; *Wania and Mackay,* 1993; *Grimalt et al.,* 2001].

In this respect, quantification of PCB loss should focus onto the processes that involve PCB destruction which essentially concern burial in deep sea sediments and degradation in the atmosphere [*Gustafsson et al.,* 1997; *Axelman and Broman,* 2001; *Wania and Daly,* 2002].

OH reaction has been proposed to be the most important parameter controlling atmospheric lifetime and long range PCB transport [*Beyer et al.,* 2000]. The importance of OH radicals on the degradation of gaseous PCBs has been assessed in laboratory experiments [*Anderson and Hites,* 1996]. Preliminary application of these reaction rate constants to environmental data resulted into a very large OH radical sink for PCBs in the Northern Hemisphere (NH), which led to question the reliability of the reaction rate constants [*Axelman and Broman,* 2001]. Recent GLOBO-POP model calculations [*Wania and Daly,* 2002] also showed the importance of PCB degradation by OH radicals but their losses were considerably lower than those calculated by *Anderson and Hites* [1996].

Gasses with long residence times have smaller variations in space and time than more reactive gases. Theoretical considerations led to propose a reverse relationship between relative standard deviation (RSD) and residence time [*Junge, 1974*].

$$T_i = 0.14/RSD_i \qquad (1)$$

where T_i is the residence time and *RSD* is the relative standard deviation of the measured concentrations of compound *i*

This relationship does not represent time fluctuations at a particular point but spatial variability of the concentrations [*Slinn, 1988*]. Thus, the measured concentrations should be representative of the whole annual period. This approach may be useful for the calculation of the residence times of gas-phase PCB since distortion effects by point source emissions [*Hamrud, 1983*] are negligible after more than two decades of PCB banning.

No attempt has been made to date to estimate the global scale atmospheric sink of PCBs based on atmospheric field data. In the present study, the global atmospheric loss of PCBs has been estimated based on new and already existing data from remote locations in both hemispheres. Latitudinal trends and longitudinal and altitudinal differences have been identified and used to obtain best estimates for congener specific global atmospheric concentrations at the different zones. Seven PCB congeners (IUPAC no 28, 52, 101, 118, 138, 153, and 180) have been taken to model the diverse behaviour of the PCB mixtures. Previously reported OH reaction rate constants and PCB field data have been used to estimate the atmospheric PCB degradation and residence time.

2. Methods

2.1. Compound selection

The environmental distribution of PCB congeners is determined by their specific vapor pressures and hydrophobicities, not by the composition of the commercial mixtures produced initially. In the present study, the congeners selected for description of the atmospheric inventory and sink, 2,4,4'-trichlorobiphenyl (PCB IUPAC No. 28), 2,2',5,5'-tetrachlorobiphenyl (PCB 52), 2,2´,4,5,5´-pentachlorobiphenyl (PCB 101), 2,3´,4,4´,5-pentachlorobiphenyl (PCB 118), 2,2´,3,4,4´,4-hexachlorobiphenyl (PCB 138), 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153) and 2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB 180), cover a wide range of these constants and are predominant in environmental samples. They are often taken as reference PCB congeners in many literature studies.

2.2. Data selection

Literature data has been selected after evaluation of sample site remoteness, sampling time, and congener specific information (Table 1). PCB concentrations on a global scale were calculated considering the globe as a remote system. Bias associated to sampling period duration or seasonality has been avoided by selection of long-term studies encompassing sampling over one year or more. Arithmetic means were calculated and incorporated into the model since they reflect better average environmental concentrations than geometric means [*Parkhurst*, 1998]. Data before 1990 was not considered. Old PCB data is often only reported as total PCB without congener specific PCB information. In addition to literature data, unpublished atmospheric concentrations from Hawaii, Moody Brook, Halley Base, Crete and Malawi Lake have been added (Table 1).

Table 1. Mean concentrations of PCB congeners in the sampling sites included in the model calculations. The tabulated values are aritmethic means of yearly sampling periods ($pg \cdot m^{-3}$).

	Latitude	Longitude	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	Reference
Punto de Hidalgo, Tenerife	28	16	24	28	18.5	7.7	8.3	8.8	2.7	van Drooge et al. (2002)
Svalbard GSC	79	12	6.2	1.9		0.4		1.3	0.4	not published
Pallas, Finland	68	24	3.2	1.9	1.5	0.5	1.4	1.5	0.9	not published
Kalix, Sweden	66	23			1.9	1.9	1.9	1.8	0.4	Agrell et al. (1999)
Bjuröklubb, Sweden	65	22			1.6	1.0	1.3	1.1	0.2	Agrell et al. (1999)
Holmögadd, Sweden	64	21			2.8	1.4	2.3	1.7	0.3	Agrell et al. (1999)
Gotska sandön	58	19			2.9	2.2	2.4	2.1	0.4	Agrell et al. (1999)
Poland, coastal	54	19			3.6	1.7	2.1	1.7	0.6	Agrell et al. (1999)
Lithuania, coastal	55	21			2.9	1.4	1.9	1.5	0.5	Agrell et al. (1999)
Hazelrigg, UK	54	-3	16	20	1.3	2.2	3.3	0.7	0.7	www.aeat.co.uk/netcen/airqual/
High Muffles, UK	54	0	18.5	13	1.6	3.8	5.9	1.8	1.8	www.aeat.co.uk/netcen/airqual/
Stoke Ferry, UK	53	1	11	14	1.6	2.5	3.8	1.0	1.0	www.aeat.co.uk/netcen/airqual/
Bayreuth, Germany	50	12	13	7.4	5.9		3.0	5.6	1.3	McLachlan M. et al. (1998)
Signy Island	-61	-46	10	6.0	2.6	0.5	0.6	0.8	0.3	Kallenborn, R. et al. (1998)
Te Wera, New Zealand	-39	175	2.9	1.2	1.7	0.7	2.0	1.4	0.2	Buckland et al. (1999)
Baring Heads, New Zealand	-41	175	3.5	1.4	1.0	0.4	0.6	0.5	0.1	Buckland et al. (1999)
Nelson Lakes, New Zealand	-42	173	2.9	1.2	1.3	0.6	0.6	0.4	0.0	Buckland et al. (1999)
Culverden, New Zealand	-43	173	3.5	1.2	0.6	0.2	0.3	0.2	0.0	Buckland et al. (1999)
Halley base, Antarctica	-76	-26	1.8	0.2			0.2		0.1	not published
Moody Brook, Falkland Islands	-52	-58	2.6	0.7			0.2		0.1	not published
Baltic	61	18		5.9				3.5	0.8	see Axelman and Broman (2001)
Wisconsin	50	-89		9.4		1.0		4.9		Manchester-Neesvig and Andren (1989)
Bermuda	34	-65	39	18	10.2			3.2	0.5	Panshin and Hites (1994)
Svalbard	79	12	2.4	2.3	1.9	0.8	1.8	1.0	0.2	Oehme (1995)
Svanvik	70	29			2.3	1.6	3.1	1.6	0.5	Oehme (1995)
Kårvatn	61	6			2.4	0.8	2.1	1.0	0.3	Oehme (1995)
Svalbard	79	12	4.3	2.5				0.6	0.2	see Axelman and Broman (2001)
Ice Island	81	-90	2.2	3.1				0.1	0.1	see Axelman and Broman (2001)
Chesapeak Bay	38	-76		7.8				9.7	1.9	see Axelman and Broman (2001)
Sault Ste. Marie, WI	47	-84	10	7.0	5.0		2.0	3.5		Monosmith and Hermanson (1996)
Saginaw. MI	44	-83	20	17	8.0		3.5	8.7		Monosmith and Hermanson (1996)
Traverse, MI	45	-86	32	24	20		5.0	12		Monosmith and Hermanson (1996)
Swedish West Coast	59	11	12	7.9	6.6	2.3	4.6	5.2	1.4	Brorstrom-Lunden et al. (1994)
Swedish West Coast	59	11	5.1	4.3				4.5	1.6	see Axelman and Broman (2001)
Alert station	82	-62	1.1	1.4				0.4	0.3	see Axelman and Broman (2001)
Finokalia, Crete	35	25	5.0	4.4	1.5	1.3		1.4	0.4	Mandalakis and Stephanou (In press.)
Hawaii	21	-156	1.6	1.3	1.1	0.2	0.7	0.6	0.2	not published
Brazzaville, Congo	-4	14	28	40				8.0	7.0	Ngabe and Bidleman, (1992)
Lake Malawi, Senga	-14	35	23	15	7.8		11	5.6	1.1	D. Muir pers. comm. (2002)

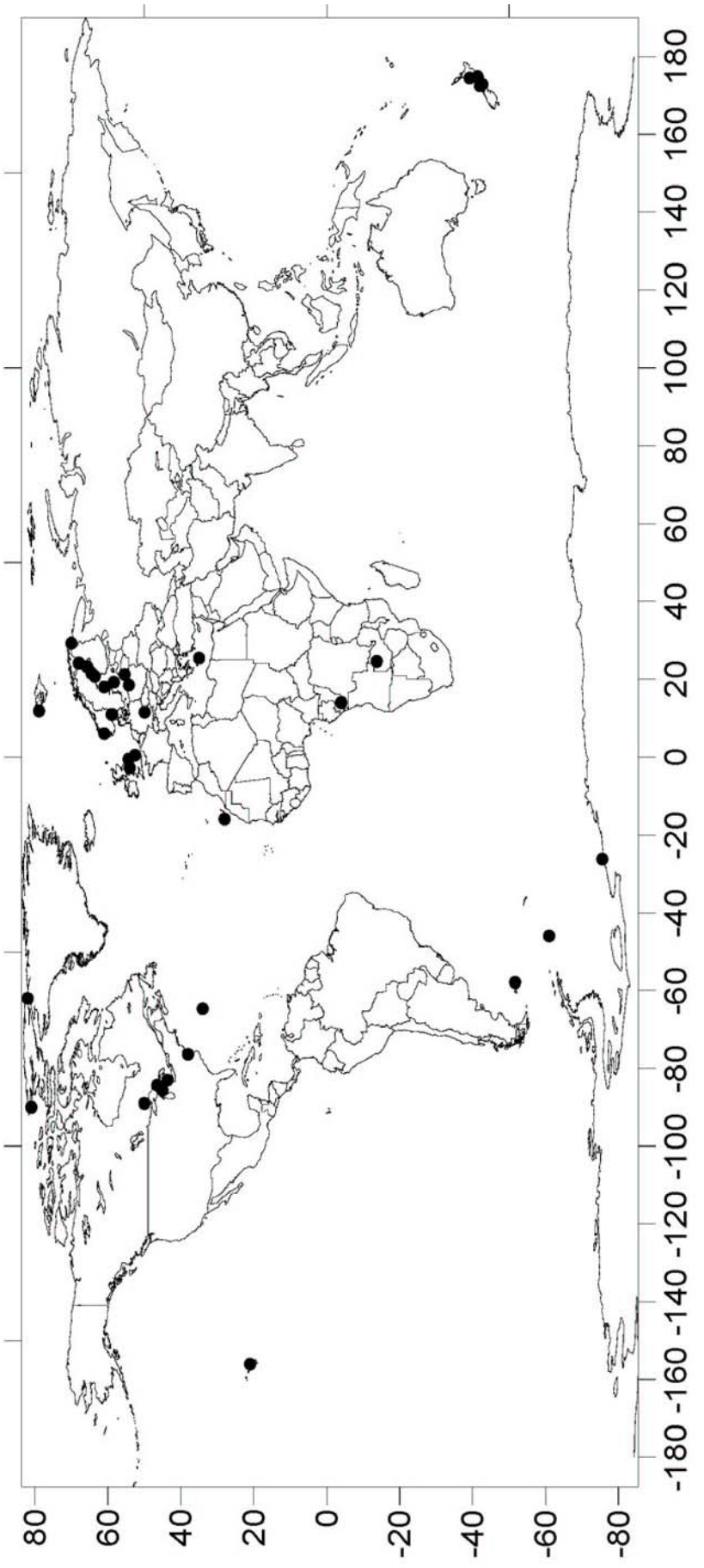

FIGURE 1. Map showing the sites from which PCB atmospheric concentrations covering more than one year period were available.

The atmospheric data selected from the literature was obtained using similar sampling and analytical methods. Sampling was performed by passing air through a glass fiber filter and then through a cartridge packed with an adsorbent material. Particulate phase bounded PCBs were retained in the filter while the gas phase PCBs were adsorbed in the cartridges. In some studies PCBs were sampled as bulk, without differentiation between gas and particulate phases. Most PCBs are present in the gas phase, the particulate phase only playing a minor role [*van Drooge et al.,* 2002; *Mandalakis and Stephanou*, 2003]. Furthermore, it is assumable that OH radical reactions on PCBs only take place in the gas phase. For these reasons, only the gas phase PCB concentrations have been considered. Introduction of the particulate phase would complicate the model unnecessarily, since a global distribution of aerosols and their organic content would be required for description of PCB partitioning between gas and particulate phase.

3. Results and discussion

3.1. Geographic distributions.

The sample sites selected for estimation of the atmospheric concentration pool are represented in Figure 1. The NH is better represented than the Southern Hemisphere (SH). Within the NH the atmospheric samples around the North Atlantic exhibit PCB levels that are more than one order of magnitude higher than the rest (Figure 2). These higher values are in agreement with the areas of higher use of these compounds [*Breivik et al.,* 2002a]. However, in all PCB congeners the concentration differences are within less than two orders of magnitude. Having in mind that the sites represented in Table 1 encompass areas as distant as western Europe and New Zealand or Antarctica, and previously reported geographical distributions of PCB use [*Breivik et al., 2002a*], the observed concentrations indicate that there is a significant degree of atmospheric mixing.

The logarithms of the concentrations in the North Atlantic area show a strong negative linear correlation with latitude between 30ºN and 80ºN for all PCBs (Figure 2 and Table 2). According to these correlations higher concentrations are found at lower latitudes. About 86% of the total historical usage of PCBs has been concentrated in a latitudinal band between 30ºN-55ºN with maxima at 40ºN [*Breivik et al.,* 2002a]. The emissions of PCBs obtained from a mass balance model which link consumption and emissions also correspond to this band but with a displacement to higher latitudes [*Breivik et al.*, 2002b]. Furthermore, the global PCB distribution in background surface soils exhibit highest concentrations in the latitudinal band between 40ºN-70ºN with maxima around 50ºN [*Meijer et al.,* 2003]. Among other factors, this northern displacement of the latitudinal soil PCB band with respect to the area of highest use in the past reflect the higher organic carbon content of soils in Scandinavia, south Canada and Siberia where PCB accumulated preferentially [*Meijer et al.,* 2003]. In any case, the highest concentrations of atmospheric PCBs at 30ºN as indicated by the linear correlations obtained from Table 1 encompasses a net transfer of PCBs from higher to lower latitudinal locations. That is, a flux in the opposite direction to that predicted in the

global distillation theory [*Wania and Mackay,* 1993]. However, this flux is not in contradiction with the assumption of the global distribution model because no condensation effects are involved.

In any case, the concentrations of these compounds in the atmosphere are distributed paralleling a temperature gradient (Table 3). Previous studies on diurnal temperature profiles have shown that PCB air concentrations exhibit positive temperature correlations involving higher daytime than night-time values [*Hornbuckle and Eisenreich,* 1996; *Wallace and Hites,* 1996; *Lee et al.,* 1998]. In Table 2, recalculation of the slopes in function of the temperature gradients (log(conc.) vs. 1/Temp (ºK)) and estimation of the phase-change enthalpies (ΔH):

$$\Delta H = \text{slope} \cdot R \cdot \ln(10) \qquad (2)$$

where R is the gas constant 8.314 $J \cdot ºK^{-1} \cdot mol^{-1}$ and ln(10) = 2.303, gives values in the order of 36-63 $kJ \cdot ºK^{-1} \cdot mol^{-1}$. These experimental enthalpies are a bit lower than the octanol-air phase transfer constants determined in laboratory experiments, 66-93 $kJ \cdot ºK^{-1} \cdot mol^{-1}$ [*Finizio et al.,* 1997], but not too different which suggests that evaporation from the ground is a significant process determining the global atmospheric distribution of these compounds. In addition to this latitudinal dependence, longitudinal differences giving rise to higher atmospheric concentrations in the areas of higher PCB use in the past [*Breivik et al.*, 2002a] are also observed. Thus, the air levels in Hawaii are about one order of magnitude lower than in the North Atlantic area (Figure 3). According to these differences, the inventories in the northern hemisphere have been calculated using two types of latitudinal dependent linear regressions. Assuming a uniform N-S latitudinal gradient, all data between 40ºE and 90ºW have been used for curve fitting of the latitudinal dependence. The resulting slopes and intercept have been used for calculation of the concentrations in this longitudinal sector and between 120º-150ºE, the area of Japan influence. In the rest of the northern hemisphere, the concentrations were calculated using the same slopes but the concentrations from Hawaii for intercept calculation. The use of these equations involves the assumption of a steady state concentration of these compounds in the atmosphere as consequence of their general release into the environment and physico-chemical structure of the atmospheric column.

In the SH, the logarithm-transformed average concentrations do not show a significant latitudinal linear dependence. From the amount of data available for this study it is not clear whether the lack of dependence is really characteristic of the SH atmospheric PCB distribution or due to lack of sufficient sampling sites. In practical terms, calculation of the PCB inventories has been performed by averaging the concentrations of all sample sites in this Hemisphere.

3.1. Maximum PCB inventory

For inventory calculations the globe surface was divided in 18 latitudinal bands of 10º uniformly distributed in the NH and SH. The atmospheric altitude in each band was taken to be 10 km and divided in 10 layers. The resulting model contained 180 boxes, each encompassing 10º of

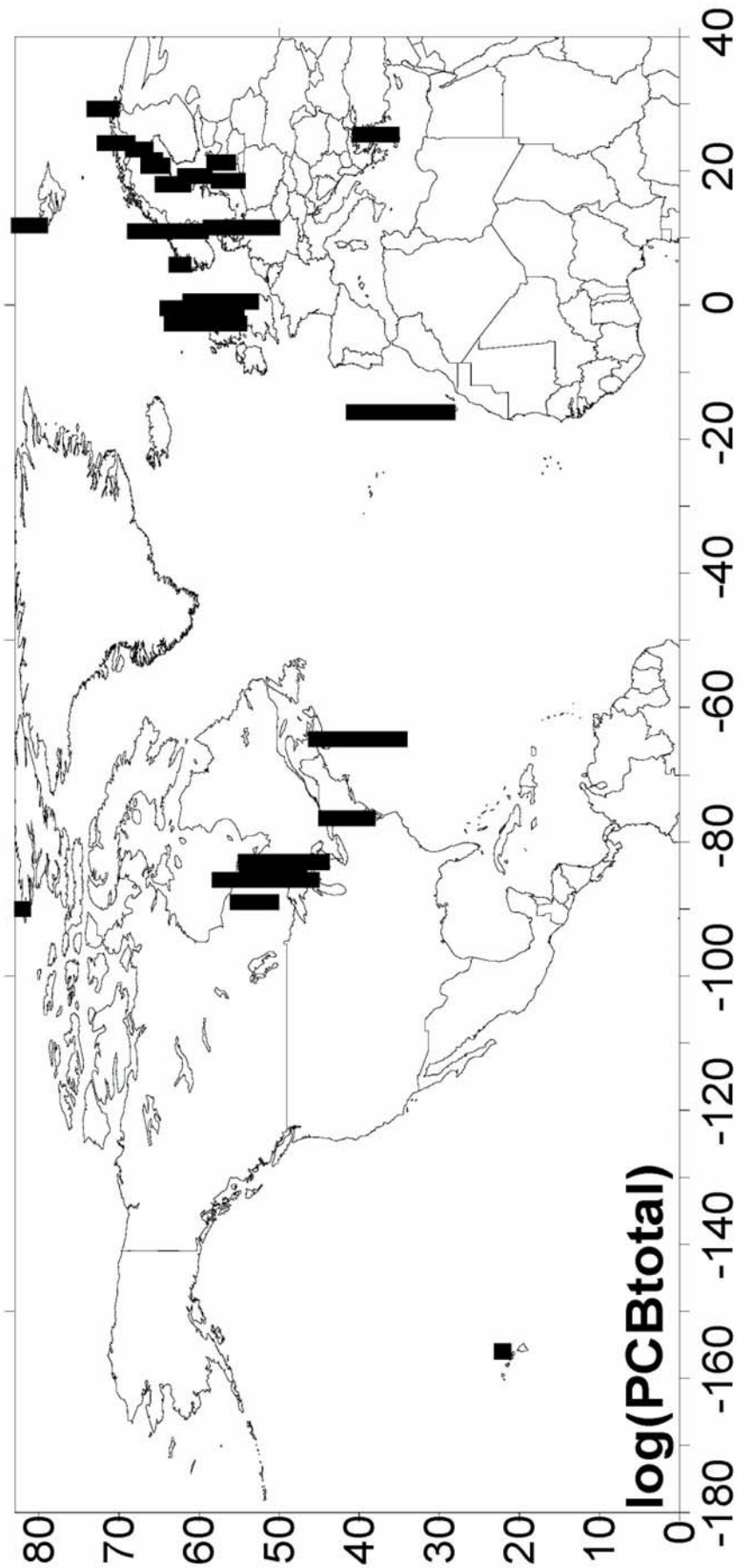

FIGURE 3. Annually-averaged total PCB concentrations in the Northern Hemisphere (log-scale)

latitude and 1000 m of height (Table 3). Similar approaches have been undertaken in previous studies such as the Globo-POP model in which the atmosphere was divided in 10 latitudinal zones and four vertical layers encompassing the lower 33 km [*Wania et al.,* 1999].

The above described latitudinal regressions for the NH (Table 2) were used to assign to each box its corresponding PCB levels. These equations predict an increasing concentration down to the equator. However, no data are available between 0-30ºN. Lower PCB emissions are expected in this latitudinal range according to the previous use of these compounds (*Breivik et al.*, 2002a). In addition, the above reported parallelism between soil organic carbon distribution and PCB accumulation [*Meijer et al., 2003*] should also involve some degree of exchange between soil and atmosphere. Considering these aspects, and the observed longitudinal differences in airborne PCB between areas from high and low use of these compounds, extrapolation of the curve fitted values between 30ºN and 80ºN to the 0ºN-30ºN sector seems inadequate. Thus, the boxes within this sector have been considered to contain PCB concentrations as those at 30ºN. With this approach, the concentrations assigned to these sectors are similar to those determined in Africa at the same latitudes but in the SH (Table 1 and Figure 2).

In the absence of other data, assumption of PCB mixing throughout the entire troposphere involves estimation of concentration-pressure dependence only due to pressure correction. As described elsewhere [*Anderson and Hites,* 1996].

$$p(h_k) = 104144\ exp(-0{,}1342 h_k) \qquad (3)$$

where p is the atmospheric pressure in Pa and h_k is the height above sea level in km at the altitude box k

Then, the PCB level for each box was calculated as

$$C_{ijk} = 10^{(a+b \cdot l)} \cdot x_{jk} \qquad (4)$$

where C_{ijk} is the average concentration of congener i at latitude j and altitude k
a is the intercept in the air concentration vs. latitude regression
b is the slope in the air concentration vs. latitude regression
l is the average latitude in the box and x_{jk} is the ratio between the mean atmospheric pressure of the box and surface pressure.

In the SH the PCB concentrations were calculated from the estimated average values.

$$C_{ijk} = Ca_{ij} \cdot x_{jk} \qquad (5)$$

where Ca_{ij} is the average air concentration of congener i in the latitude sector j and C_{ijk} and x_{jk} are defined as in (3).

The results of these inventory calculations are summarized in Table 4. Consistently with the concentration differences observed between NH and SH samples, the amount in the former is more than two times higher. The average estimate of PCB concentrations resulting from this approach is 13 pg·m^{-3} which is sensibly lower than the estimated of 200 pg·m^{-3} from *Anderson and Hites* [1996].

Table 4. Global PCB atmospheric inventories and sinks for different options assuming complete concentration mixing or vertical gradient in the troposphere (10 km).

Maximum								
PCB Congener No.	**28**	**52**	**101**	**118**	**138**	**153**	**180**	**ΣPCB**
Inventory NH (tons)	14	10	5	2,2	3,3	4,0	0,9	40
Inventory (tons)SH	9	5	3,6	0,7	2,8	2,1	0,4	24
Total Inventory	**23,2**	**15,3**	**8,4**	**2,8**	**6,1**	**6,1**	**1,2**	**63**
OH sink NH (tons·yr^{-1})	996	453	129	58	54	69	9	1768
OH sink SH(tons·yr^{-1})	552	186	86	16	42	32	3	918
Total OH degradation (tons·yr^{-1})	**1548**	**639**	**215**	**74**	**96**	**101**	**13**	**2686**
Vertical gradient								
PCB Congener No.	**28**	**52**	**101**	**118**	**138**	**153**	**180**	**ΣPCB**
Altitudinal coefficient (d; km^{-1})	-0.40	-0.45	-0.27	-0.24	-0.26	-0.28	-0.068	
Inventory NH (tons)	6,1	4,0	2,9	1,5	2,1	2,3	1,1	20
Inventory SH (tons)	3,9	1,9	2,2	0,5	1,7	1,3	0,5	12
Total Inventory	**10,0**	**5,9**	**5,1**	**1,9**	**3,8**	**3,6**	**1,6**	**32**
OH sink NH (tons·yr^{-1})	446	185	83	41	37	44	11	846
OH sink SH(tons·yr^{-1})	234	71	54	11	27	20	4	422
Total OH degradation (tons·yr^{-1})	**680**	**256**	**137**	**52**	**64**	**63**	**15**	**1268**
Other budgets (tons)								
Soils[a]	**190**	**210**	**170**	**400**	**530**	**1200**	**580**	**3280**
Continental shelf sediments[b]	**460**	**700**				**1200**	**760**	
Total production[c]	**57000**	**38000**	**32000**	**43000**	**25000**	**38000**	**14000**	**247000**

Footnotes: [a]from [Meijer et al., 2003]; [b]from [Jonsson et al., 2003]; [c]from [Breivik et al., 2002a]

3.2. Vertical-gradient inventory

In this second option, the vertical PCB distribution is assumed to represent a vertical gradient in addition simple air dilution. The vertical profile has been extrapolated from the one measured by congener specific PCB analysis in the island of Tenerife at 2367 m and sea level [*van Drooge et al.,* 2002]. These vertical profiles show a higher altitudinal decrease for the less chlorinated PCBs than for the higher chlorinated congeners. The observed differences are consistent with other independent studies performing airplane measurements at 500 and 3000 m above sea level [*Knap*

and Binkley, 1991]. An exponential decline function was assumed with increasing altitude. Now, the PCB concentrations for each box, C_{ijk}, in the NH and SH can be calculated as follows

$$\text{NH: } C_{ijk} = 10^{(a+b\cdot l)} \cdot e^{d\cdot h} \quad (6)$$

$$\text{SH: } C_{ijk} = Ca_{ij} \cdot e^{d\cdot h} \quad (7)$$

where d is the coefficient for the altitudinal PCB level decline (Table 5) and the other terms are defined as in the previous equations.

Table 5. Altitudinal coefficient, pre-exponential factors and activation energies (E_a) for the reaction of PCB congeners with hydroxy radicals (after Axelman and Broman, 2001). R = 8.314 J $^oK^{-1}$ mol^{-1}.

Congener No.	Altitudinal Coefficient (d; km^{-1})	Pre-exponential factor (s^{-1})	E_a/R (^oK)
28	-0.40	57	959
52	-0.45	108	1265
101	-0.27	205	1571
118	-0.24	205	1571
138	-0.26	389	1877
153	-0.28	389	1877
180	-0.068	739	2183

Once the PCB concentrations for each box are defined, the inventories can be calculated as follows

$$M_{ijk} = C_{ijk} \cdot V_{jk} \quad (8)$$

where M_{ijk} stands for the amount of congener i in the box jk (in kg)
V_{jk} is the volume of box jk and C_{ijk} is defined as in (6) and (7)

In this approach, a stronger vertical gradient is observed for the lighter than for the heavier congeners (Figure 4). The estimated inventories represent about half of the amounts obtained in the previous inventory calculations (Table 4). As in the previous case (maximum amount) the value for the NH is two times higher than in the SH. The average estimate of PCB concentrations corresponding to this approach is 6.5 $pg\cdot m^{-3}$. These values compare well to those obtained in the model of *Wania and Daly* [2002] who estimated a global concentration interval for 1999 ranging between 0.5 and 55 $pg\cdot m^{-3}$.

The resulting inventories are about 0.3-5% of the inventories calculated for the PCB amounts stored in soils (Table 4; [*Meijer et al.,* 2003]). As expected the atmospheric budgets of the more volatile congeners, e.g. #28, 52 and 101, represent higher relative amounts, 3-5%, of the soil budgets than those of the less volatile compounds, e.g. 0.3-0.7% for #118, #138, #153 and #180.

Comparison to the PCB amounts stored in the continental shelf sediments (Table 4; [*Jonsson et al.,* 2003]) show even lower proportions (0.2-2%) since the calculated budget of PCBs in this environmental compartment is even higher than the one in soils.

3.3. Reaction rates and sinks due to OH radicals

The concentrations of OH radicals in the global troposphere are difficult to measure due to the short lifetime and low levels. However, there have been some attempts to give annual global tropospheric means [*Spivakovsky et al.,* 2000; *Hein et al.,* 1997]. In the calculations of *Spivakovsky et al.* [2000] the mid troposphere OH radical concentrations range between 23.4 $x10^5$ molecules·cm^{-3} in the tropics and 0.9 $x10^5$ molecules·cm^{-3} at the North Pole, with mean concentrations of 8.5 $x10^5$ molecules·cm^{-3} and 8.8 $x10^5$ molecules·cm^{-3} in the NH and SH, respectively. The approach of this study was used to obtain latitudinal and altitudinal OH radical concentrations.

As described in *Axelman and Broman* [2001] the OH reaction rates k_{OH} (s^{-1}) for PCBs were based on an Arrhenius temperature dependence equation for each congener (Table 5) using the raw data from *Anderson and Hites* [1996].

$$k_{OHijk} = 8.2865\ exp(0.6415\ Cl_i)\ exp(-(306.05 \cdot Cl_i + 40.714))(1/T_{boxjk}) \qquad (9)$$

where Cl_i is the number of chlorine substituents in each congener *i,* and T_{boxjk} is the average temperature of the box *jk* (ºK),

Calculation of k_{OHjki} from equation 9 was performed using the average annual ambient temperature at the surface of each box and then decreasing at 5ºC km^{-1}. The OH radical concentrations were estimated from the model of *Spivakovsky et al.* [2000]. Highest potential degradation rates $k_{OHijk} \cdot [OH]_{jk}$ were obtained in the warmer zones, like the tropics (Figure 4). However, the calculations also show that in this warm area higher degradation potential is found at higher altitudes due to the higher amounts of OH radicals (Figure 4).

The sink of each PCB congener (*i*) in each box (*jk*) (S_{ijk} (kg y^{-1})) was calculated as

$$S_{ijk} = k_{OHijk} \cdot [OH]_{jk} \cdot M_{ijk} \qquad (10)$$

where k_{OHijk}, $[OH]_{jk}$ *and* M_{ijk} are calculated as defined above.

All PCB congeners show highest degradation rates at low latitudes (0-30ºN/S; Figure 4). The lighter PCB congeners are degraded at higher rate near surface. However, highly chlorinated congeners such as #180 are degraded at higher extend at altitudes around 1-4 km due to their lower vertical gradient

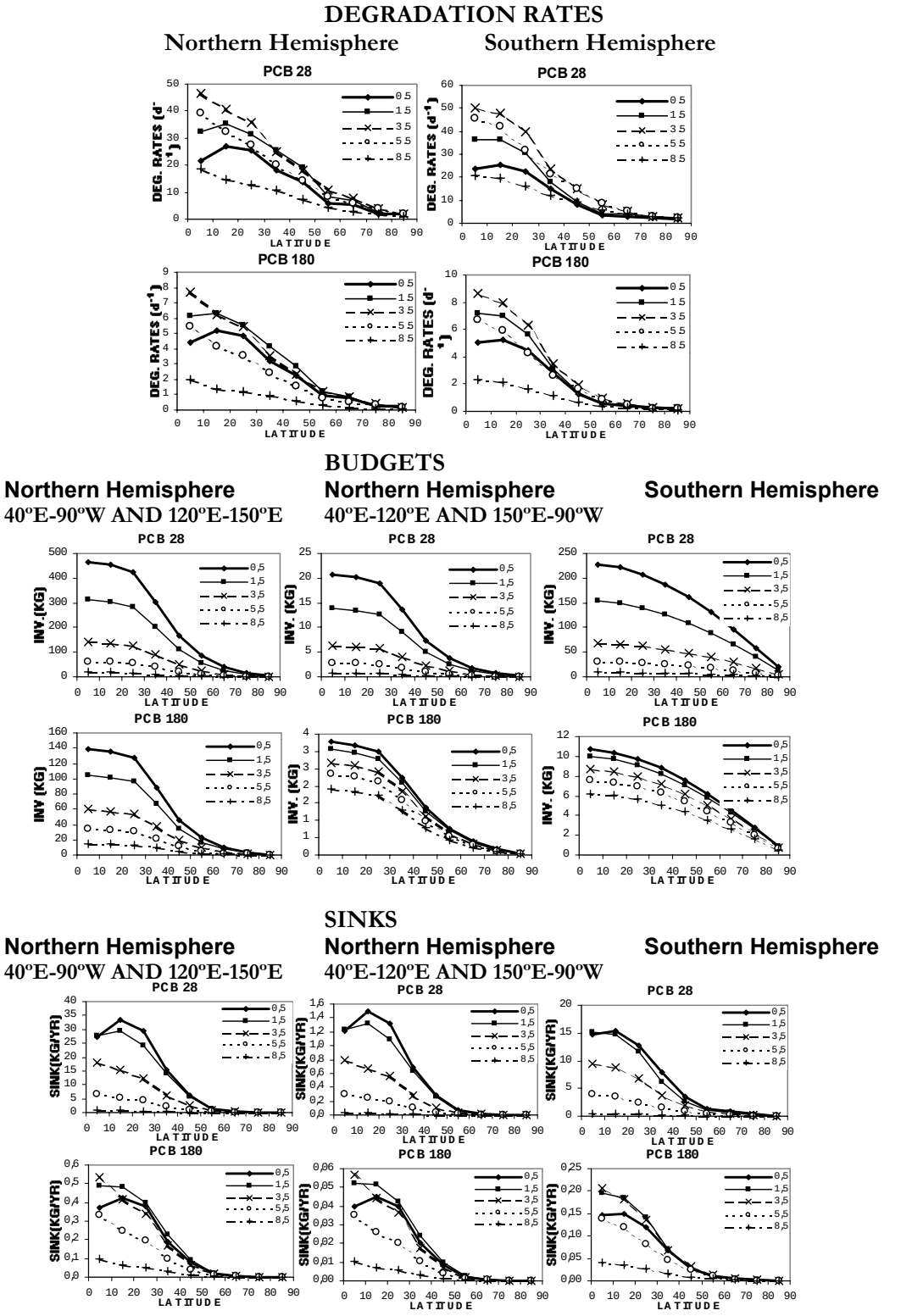

FIGURE 4. Examples based on PCB congeners #28 and #180 of calculated degradation rates, budgets and sinks of the mass balance box model assuming a vertical gradient (see text). According to the differences between PCB concentrations (Table 1) the planet is divided in three regions, two in the northern hemisphere (40ºE-90ºW and 120ºE-150ºE) and (40ºE-120ºE and 150ºE-90ºW) and one in the southern hemisphere (whole).and the higher OH concentrations at these elevations

(Figure 4). In any case, the heavier PCB congeners are degraded at a much lower rate (45 times for #28 than #180; Table 4).

In the vertical gradient model the sinks, 1300 $t \cdot y^{-1}$, are about half than those in the maximum inventory, 2700 t y^{-1} (Table 4). Although these amounts are significant, they are much lower than the sink predicted by *Anderson and Hites* (1996) who estimated 8271 t y^{-1} for total PCBs. In contrast, the estimated loss in the present study, e.g. vertical gradient, is still six times higher than the 218 t y^{-1} estimated by *Wania and Daly* (2002).

In any case, the sinks obtained in the present study are huge in comparison to the total inventories. Thus, in the case of congener #180 they are more than nine times higher than the global atmospheric inventory and in the case of congener #28 they are 68 times higher. These large numbers involve the need of a high emission flux of PCBs to the atmosphere in order to maintain the observed concentrations (Table 1). Thus, in the case of PCB #28 it involves an approximate renewal time of five days. This period is of 39 days for PCB #180.

The sink estimates reported in Table 4 have been obtained by combination of the information derived from air concentration measurements and experimental models for OH reaction rates. As indicated above, there are uncertainties in the concentration values, namely for large world areas from which no reliable data are available. However, the consistency of the data already obtained from different studies (Table 1) precludes that major differences in the atmospheric pool such as one order of magnitude could be expected from a model derived with a larger number of determinations. On the other hand, equation 9 used for estimation of the degradation rates compares well to the experimental values obtained in Finokalia (Crete, Greece). Thus, similar k_{OH} rates have been obtained based on the experimental measurement of PCB depletion and OH radical species [*Mandalakis et al., 2003*].

Overall, the data summarized in Table 4 points to a major PCB emission process to account for the large photochemical degradation in the atmosphere. These emissions must originate from environmental compartments other than soils or continental shelf sediments. Otherwise, the volatile PCB congeners contained in these reservoirs would be eliminated in short periods (a few years) if they would be the only source of PCB to the atmosphere.

The sink values of Table 4 are considerably higher than the estimated emissions based on a global mass balance of PCB production, historical usages, disposal and accidental release [*Breivik et al., 2002b*]. Thus, the 70 years averaged release rate of PCB#28 is 12 $t \cdot y^{-1}$(minimum and maximum values 0.65 and 167 $t \cdot y^{-1}$, respectively) whereas the atmospheric sink of this congener is 680 $t \cdot y^{-1}$ (Table 4, vertical gradient). Similarly, for PCB#180 the average emission rate is 1.3 $t \cdot y^{-1}$ (minimum and maximum values 0.083 and 15 $t \cdot y^{-1}$, respectively) [*Breivik et al., 2002b*] whereas the sink rate estimated in this study is 15 $t \cdot y^{-1}$ (Table 4, vertical gradient). The differences between estimated emissions [*Breivik et al., 2002b*] and sinks are therefore significant. Higher differences are found as lower is the degree of chlorination of the PCB congeners which reflects the higher degradation

sinks at lower degree of chlorine substitution. Thus, the PCB#28/180 sink rate is 45 whereas the PCB#28/180 average emission rate is 28.

In addition, the finding of the highest PCB concentrations in the tropical zones where degradation rates and occurrence were highest involve that PCB transport from the areas of highest use to the tropics must have been very significant.

3.4. PCB loss by atmospheric residence times

The RSD from the data series summarized in Table 1 have been calculated. Average values corresponding to NH and SH have been obtained. The RSD due to analytical error have been estimated from the results of the GLOBAL-SOC intercalibration exercise on atmospheric PCB performed in 1998. The RSD corresponding to the pooled results of IIQAB-CSIC and the Lancaster University have been taken as reference. For most PCB congeners they involved values in the order of 20% of the field data RSD. These analytical RSD have been subtracted from the air concentration RSD values obtained from Table 1 and the resulting dispersion values have been used to obtain residence times using equation (1).

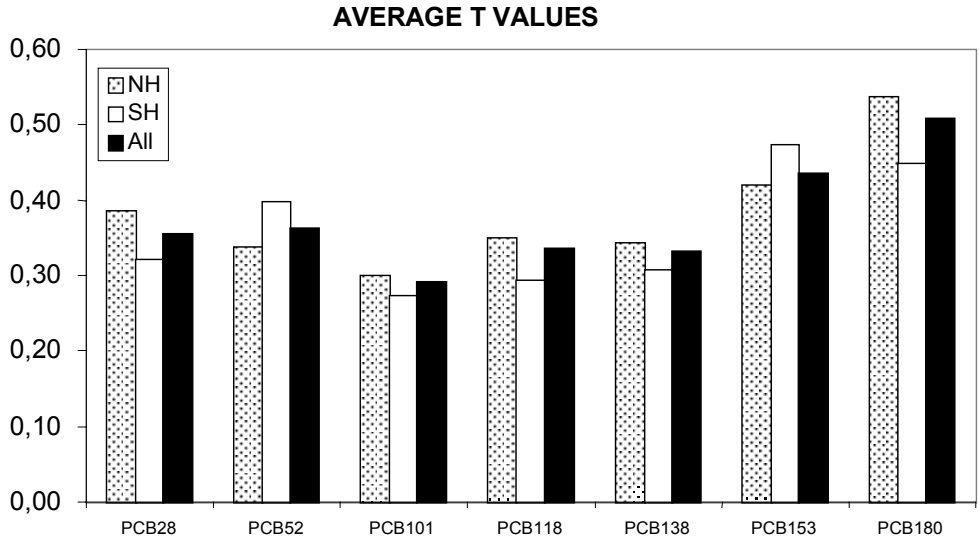

FIGURE 5. Average residence times for the PCB congeners calculated from the databases reported in Table 1.

The resulting values for the NH and SH are shown in Figure 5. Slightly lower loss rates for the more chlorinated congeners are found, namely PCB#153 and PCB#180. The differences between NH and SH are small. Accordingly, all values have been averaged and the means used for the calculation of PCB losses.

The sink of each PCB congener (i) in each box (jk) (S_{ijk} (kg y^{-1})) was calculated as

$$S_{ijk} = 1/T_i \cdot M_{ijk} \quad (11)$$

where T_i are reported in Figure 5 and M_{ijk} are calculated as defined above in equation (8).

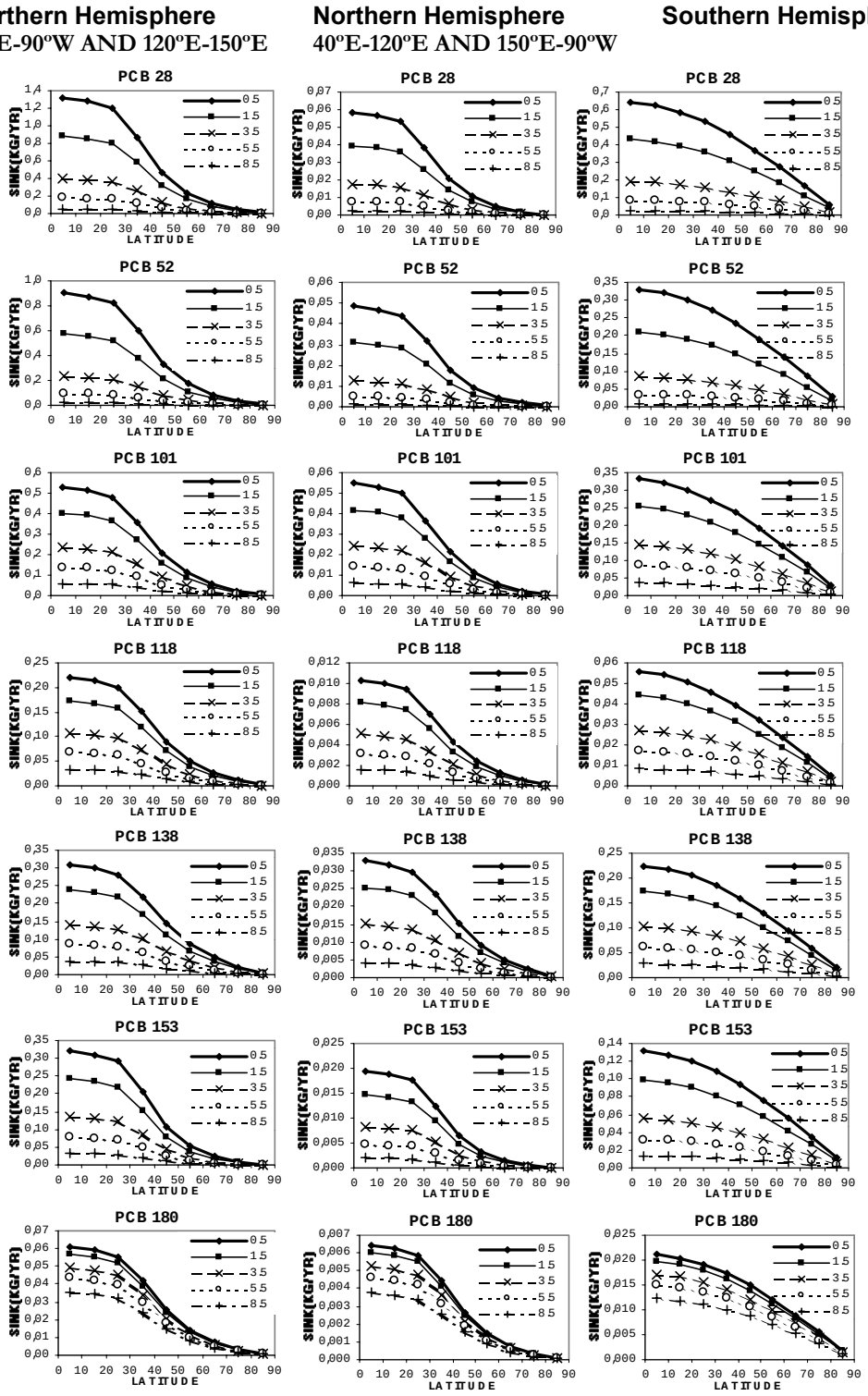

FIGURE 6. Examples based on PCB congeners #28 and #180 of calculated degradation rates, budgets and sinks of the mass balance box model assuming a vertical gradient (see text). According to the differences between PCB concentrations (Table 1) the planet is divided in three regions, two in the northern hemisphere (40ºE-90ºW and 120ºE-150ºE) and (40ºE-120ºE and 150ºE-90ºW) and one in the southern hemisphere (whole).

All PCB congeners show highest degradation rates where they are found in higher concentration. That is, at low latitudes and altitudes (Figure 6). The altitudinal differences are higher for the less than the more chlorinated PCB congeners. In the vertical gradient model the sinks, 90 $t \cdot y^{-1}$, are about half than those in the maximum inventory, 180 t y^{-1} (Table 6). Although these amounts are significant, they are much lower than the sink predicted by *Anderson and Hites* (1996) who estimated 8271 t y^{-1} for total PCBs and even lower than those estimated by *Wania and Daly* (2002), 218 t y^{-1}. The estimated values are also consistent with the estimated emission values reported by Breivik et al (*2002b*) based on historical emissions. As shown in Table 6, the loss values of all PCB congeners estimated in the present study fall within the range of average PCB emission for the 1930-2000 years period.

Table 6. Global PCB atmospheric inventories and sinks for different options assuming complete concentration mixing or vertical gradient in the troposphere (10 km).

Maximum								
PCB Congener No.	**28**	**52**	**101**	**118**	**138**	**153**	**180**	**ΣPCB**
Inventory NH (tons)	14	10	5	2.2	3.3	4.0	0.9	40
Inventory (tons)SH	9	5	3.6	0.7	2.8	2.1	0.4	24
Total Inventory	**23**	**15**	**8.4**	**2.8**	**6.1**	**6.1**	**1.2**	**63**
NH loss ($tons \cdot yr^{-1}$)	40	29	16	6	10	9	2	110
SH loss ($tons \cdot yr^{-1}$)	26	13	12	2	8	5	1	67
Total Loss ($tons \cdot yr^{-1}$)	**65**	**42**	**29**	**8**	**18**	**14**	**2**	**180**
Vertical gradient								
PCB Congener No.	**28**	**52**	**101**	**118**	**138**	**153**	**180**	**ΣPCB**
Altitudinal coefficient (d; km^{-1})	-0.40	-0.45	-0.27	-0.24	-0.26	-0.28	-0.068	
Inventory NH (tons)	6.1	4.0	2.9	1.5	2.1	2.3	1.1	20
Inventory SH (tons)	3.9	1.9	2.2	0.5	1.7	1.3	0.5	12
Total Inventory	**10**	**5.9**	**5.1**	**1.9**	**3.8**	**3.6**	**1.6**	**32**
NH loss ($tons \cdot yr^{-1}$)	17	11	10	4	6	5	2	56
SH loss ($tons \cdot yr^{-1}$)	11	5	8	1	5	3	1	34
Total Loss ($tons \cdot yr^{-1}$)	**28**	**16**	**17**	**6**	**12**	**8**	**3**	**90**
Other budgets (tons)								
Soils[a]	**190**	**210**	**170**	**400**	**530**	**1200**	**580**	**3280**
Continental shelf sediments[b]	**460**	**700**				**1200**	**760**	
Total production[c]	**57000**	**38000**	**32000**	**43000**	**25000**	**38000**	**14000**	**247000**
Average emissions (1930-2000)[d] ($tons \cdot yr^{-1}$)	**0.65-170**	**0.35-83**	**0.19-41**	**0.26-43**	**0.15-32**	**0.16-37**	**0.083-15**	**1.8-420**

Data from [a][Meijer et al., 2003], [b] [Jonsson et al., 2003], [c] [Breivik et al., 2002a], [d] [Breivik et al., 2002b]

In contrast, extrapolation at a global scale of the PCB deposition values measured in remote sites such as Teide (Canary Islands; *van Drooge et al., 2000*), Pyrenees, Alps and Norway [*Carrera et al., 2002*] and the Swedish west coast [*Brorstrom-Lunden et al., 1994*] gives higher loss values (390 t y^{-1} for the sum of the seven PCB considered in this study) than those estimated with the present model.

These higher deposition values are perhaps reflecting that all the sites from which yearly deposition data are available correspond to the sector between 30ºN and 60ºN and 40ºE and 90ºW. The one having highest PCB use in the past [*Breivik et al, 2002b*] and highest PCB accumulation in soils [*Meijer et al., 2003*].

The sink estimates reported in Table 6 have been obtained by combination of the information derived from air concentration measurements and experimental models for OH reaction rates. As indicated above, there are uncertainties in the concentration values, namely for large world areas from which no reliable data are available. However, the consistency of the data already obtained from different studies (Table 1) precludes that major differences in the atmospheric pool such as one order of magnitude could be expected from a model derived with a larger number of determinations.

Overall, the data summarized in Table 6 points to a major PCB emission process to account for the large loss in the atmosphere. These emissions involve a renewal time of about four months for the global burden of atmospheric PCB. As indicated above, this rate is consistent with the average emission losses estimated from the PCB use in the past. Emissions from soils or continental shelf sediments are also feasible sources for the observed concentrations of PCB in the atmosphere.

4. Conclusions

The obtained results show large differences between the sink of PCBs by OH radicals and the estimated atmospheric residence time. The observed differences in vertical gradient between PCB congenrers and the differences in reaction rates between PCBs and OH radicals indicates that the OH reactions have influence on the less chlorinated PCBs. However, the reaction rates may not be the ones calculated by Anderson and Hites (1996b). Application of the Junge model to estimate the tropospheric residence time of PCBs does not resolve the question which fraction is removed irreversibly from the troposphere (photo-degradation) and which fraction is removed reversibly (deposition). Deposited PCB could re-volatilise and form part again of the troposphere. Application of the Anderson and Hites (1996b) reaction rates may distinguish for the loss of PCBs from the troposphere, however, the very high PCB loss is not realistic in compare with other loss process and emission data. Moreover, there are no evidences in environmental data that such a depletion takes place. Highest atmospheric PCB concentrations are calculated in the tropical zone, without having data from this area. Since this area occupies a large volume in the Global inventory it is of importance to obtain data from remote tropical sites. The importance of this area is furthermore underlined by the fact the highest OH radical concentrations are estimated here. One way or another, the findings of the presented study suggest that there is still a wide gap of knowledge in the understanding of the atmospheric fate of these ´well-studied´ compounds.

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Chapter 7 Discussion

Chapter 7. Discussion

7.1 Atmospheric transport and fate of POP in the subtropical troposphere

7.1.1 Organochlorine compounds

The subtropical troposphere is here represented by the Atmospheric Observatory of Izaña. The concentrations of the organochlorine compounds are rather uniform and the troposphere is showing a well mixing of these pollutants. All OC show concentrations that are in the lower range of atmospheric samples from remote areas. The majority of them were detected in the gas phase and only the more chlorinated PCBs exhibit temperature dependence with shallow slopes in the plot of concentration versus inverse of temperature. Absence of temperature dependence or shallow slopes in the plots is related to long range transport (Wania et al., 1998). This is consistent with the results of the back-trajectories of the collected atmospheric samples showing that the origin of the air masses has no relevance for the load of contaminants. These results indicate that mixing and weathering processes like photo-degradation and deposition have homogenised the content of OC in the air mass. HCB is the individual organochlorine compound with the highest concentration, which is coherent with its theoretically long atmospheric life time, due to its high vapor pressure and resistance against degradation. Some evidence is found for the possible degradation of PCBs by OH-radicals. The levels of OC found at sea level (Punta de Hidalgo) are significantly higher for most of the compounds. The fact that tri- and tetra-CBs are dominating the PCB composition near sea level, while the penta-CBs dominate the air masses above the inversion layer, points to a possible effect of degradation by OH-radicals on the less chlorinated, and more reactive, PCBs during long-range atmospheric transport.

In contrast to the homogeneous atmospheric OC composition, the atmospheric deposition shows variability that is related to the mode of deposition. In the dry periods (dry deposition only and gas exchange with surface) there is a relatively constant deposition flux. This flux is in the lower range of the deposition observed in other remote areas. In episodes of wet deposition significantly higher loads are observed for most compounds. The increase is largest for the more volatile and water-soluble compounds, such as HCHs and less chlorinated PCBs. Since these compounds are predominantly detected in the gas phase, findings illustrate that there is an efficient exchange of gas phase to rain for these compounds. Correction for the average annual precipitation modes at the Atmospheric Observatory of Izaña shows that the episodes of wet deposition are responsible for 90% of the total deposition of HCHs, while this is 76% and 82% for HCB and 4,4'-DDE, respectively, and about 60% for the more volatile PCBs (#18, #28, and #52). For the less volatile PCBs (#70 and more chlorinated) the wet deposition represents between 40% and 50% of the total annual deposition load in the free troposphere in this part of the North Atlantic Ocean.

7.1.2 Polycyclic aromatic hydrocarbons

The analysis of the PAH in the free troposphere show very low concentrations of these compounds. They are in the lower range of those found in other remote areas. This is directly related to the remoteness of the sampling site, the absence of local or regional pollution sources and the influence of weathering processes during long-range atmospheric transport. The results also illustrate a great homogeneity in individual PAH composition. Similar distributions are found in other remote areas and are characteristic for air masses after long-range transport and independent of emission sources (Fernández et al., 2002).

Paralleling the differences in atmospheric composition, lower PAH concentrations were observed in soils above the inversion layer (1800m-3400m), than soils within the inversion layer (10m-1800m). The relative composition of PAH in the gas phase and in soils suggests that the mechanisms of input and conservation of PAH in soils is different within and above the inversion layer. In the former case soils are characterised by a high organic carbon content due to the support of local vegetation, while in the second soils lack the input of organic carbon from local vegetation.

The soil-air partitioning model based on the organic carbon content of the soil and the octanol-air partitioning coefficient (K_{oa}) predicts very well the distribution of the studied PAH within the inversion layer, while this model underestimates the partitioning coefficient (K_p) obtained empirically. Incorporation of the soot-carbon model ($f_{sc} \cdot K_{sa}$) to the soil-air partitioning model shows that the predicted K_p is in good agreement with the measured K_p above the inversion layer. These findings show that the partitioning of PAH between air and soil depends largely on the composition of the soils. Dachs and Eisenreich (2000) proposed that if the organic fraction (f_{OC}) is more than 2 orders of magnitude higher than the soot-carbon fraction (f_{SC}), absorption of PAH into organic matter is the dominant sorption mechanism. In fact, this is the case in the soils located within the inversion layer of the lower part of the island. Abundant vegetation and high organic matter content may cover the soot-carbon content in these soils. Conversely, in the soils situated above the inversion layer, f_{SC} is relatively high in comparison to the f_{OC}. Therefore the adsorption of PAH to soil SC is the dominant process. This will also be the probable scenario for soils poor in organic matter that receive deposited aerosols, such as the soils in high-mountain areas. In fact the implication of the soot-carbon model to the gas-particle partitioning of PAH in atmospheric samples from European high-mountain areas show that soot-carbon is the main factor of the long-range atmospheric transport of particle-bounded PAH to these areas (Fernández et al., 2002).

7.2 Atmospheric transport and fate of POP in European high-mountain areas

7.2.1 Organochlorine compounds

7.2.1.1 Active air sampling: HiVol

The relative composition of OC in the atmospheric samples determined by HiVol pumping in the High Tatras (Skalnate Pleso) and the Central Pyrenees (Estany Redon) is very similar. Most of the studied compounds are present in the gas phase, which is consistent with observations in other studies, like the free-troposphere on Tenerife (see article 1 and 7.1). At both sites HCB, which is only present in the gas phase, is the OC with the highest individual concentration. This compound is followed by γ-HCH, α-HCH, 4,4,'-DDE, and the individual PCB congeners. In terms of concentrations γ-HCH was the pre-dominant OC in the particulate phase. The less volatile PCB congeners, e.g. #149, #118, #153, 138, and #180, had similar or higher concentration in the particulate phase than in the gas phase, which is in agreement with reported gas-particulate phase distributions (Pankow, 1987).

The atmospheric levels observed near the lakes are in the lower range among those previously observed in other remote sites. Only PCB congeners and 4,4'-DDE show lower concentrations in the Arctic (Oehme et al., 1995). γ-HCH and endosulphanes observe high levels in the warmer periods. The ratios of α/γ-HCH and α/β-endosulphanes indicate that these high levels are directly related to the application of the compounds for agricultural purposes on the European continent. Thus, their observed atmospheric variability is related to use. Other OC compounds show an atmospheric variability that is related to ambient temperature. This was also observed for the OC in atmospheric deposition and lake waters in the European high-mountains (Vilanova et al., 2001c; Carrera et al., 2002). However, in the atmosphere this relationship was only significant for the less volatile compounds, e.g. PCB52 and more chlorinated PCB congeners and 4,4'-DDE.

Better correlation coefficients between concentration and reciprocal of temperature were found for Skalnate Pleso than for Estany Redon. Atmospheric gas phase concentrations drop with decreasing ambient temperatures. This points to evaporation/condensation effects or solid-gas phase exchange as the main factors for OC occurrence in the gas phase. Calculated pseudo-enthalpies range between 27 and 55kJ mol^{-1} for the individual OC in Skalnate Pleso with a small error for the less volatile PCB congeners and 4,4'-DDE. These values are lower than the laboratory-derived enthalpies, which indicates that long-range atmospheric transport (LRAT) is the main mechanism controlling the atmospheric OC (Wania et al., 1998).

Back-trajectories in Skalnate Pleso show that the oceanic air masses contain lower OC levels than the air masses that have travelled for a longer time over the European continent. Only HCB has similar concentrations in both cases. These higher concentrations in the continental group of samples is consistent with emissions from the continent, where some OC were produced and

used in the past (PCBs and 4,4'-DDE) and others are still being used (HCHs and endosulphanes). Although, the low pseudo-enthalpies point to LRAT as the main factor controlling the atmospheric gas phase, the European continent may be a source for these compounds. In the case of the back-trajectories of the air masses sampled near Estany Redon, the differences between continental and oceanic trajectories is less defined, which is due to its situation on the periphery of the European continent. Classification of the samples shows that the continental air masses contain higher levels for most of the OC than the oceanic air masses. However, the differences are not as clear as they were in the case of Skalnate Pleso. Air masses from high altitudes (>6000m) show very low levels. Besides lower ambient temperatures these trajectories are more exposed to weathering processes and further away from potential emission sources. High altitude air masses and air masses with an oceanic trajectory are more related to the colder season, which is in coincidence with a more stable atmospheric situation in winter than in summer (Barry, 1992). The transport of OC to these high-mountain areas is related to LRAT, but the origin of the compounds is mainly related to surface sources located in Europe.

7.2.1.2 Passive air sampling:

7.2.1.2.1 *Pinus uncinata*

Needles of *Pinus uncinata* have demonstrated to be very useful in the determination of atmospheric PCB levels. The method is cheap and fast and can be applied on a large spatial scale and repeated temporally. *Pinus uncinata* is the uppermost growing tree species in the Pyrenees with growing heights up to 2400m. The analysis of the leaves on its PCB content show that the highest levels of most of the PCB, except PCB#28, were found at the highest sample site (e.g. Estany Redo, 2250m) and at lowest ambient temperature. This finding indicates that the temperature is the main factor controlling the concentrations in pine leaves. Probably temperature also controls the solid-gas phase exchange, as it did in fish muscle and sediments from high-mountain lakes (Grimalt et al., 2001; Vives et al., 2004). This result is in agreement with the global distillation theory (Wania and Mackay, 1993). This relationship disappears for most of the PCB congeners, except the less volatile one, PCB180, when pine needle concentrations were corrected for lipid content. Pseudo-enthalpies obtained from the plots of the log dry weight concentrations versus inverse of the ambient temperature indicate that the values observed in the pine needles are in good agreement with the laboratory derived enthalpies of vaporisation. The pine needle-air partitioning coefficient (K_{pa}) exhibits a good relationship with the octanol-air partitioning coefficient (K_{oa}). However, K_{pa} shows a stronger temperature dependence than K_{oa}, which is also observed in other species (Kömp and McLachlan, 1997a). In this sense the K_{oa} can not automatically be used in model calculations to obtain atmospheric levels from plant leaf concentrations. Estimations of atmospheric PCB levels at different altitudes using the obtained K_{pa} temperature relationship and the pine needle

concentrations at these altitudes show that atmospheric levels decrease slightly with increasing altitude, which is consistent with atmospheric measurement with HiVol pumping in January 2003 at 2250m (Estany Redon) and 1600m (CRAM). Moreover, the estimated atmospheric levels are in the same range as those obtained by conventional HiVols.

7.2.1.2.2 SPMDs

Semipermeable Membrane Devices (SPMDs) have demonstrated in the study near Estany Redon that they can be used as monitoring devices for atmospheric OC levels. In a sense, they can be compared with pine needles, as they have a large surface/volume ratio. However, due to the fact that SPMDs are only exposed to the atmosphere over a period of few months, not all OC will achieve equilibrium. The uptake of chemical compounds has to be calculated using SPMD-air partitioning coefficients (K_{sa}) and assuming that the exchange is boundary controlled. This could introduce a number of errors that may have influence on the finally calculated atmospheric levels by SPMDs. In contrast to the observed OC concentrations in pine needles, the SPMDs show very similar OC amount along a vertical gradient of 1000m, between 1600m and 2600m. Sampling rates of OC are modelled by using the calculated value of the performance reference compound PCB155. These values, together with physico-chemical properties of HCB and PCB congeners, were used to estimate the atmospheric levels at 1600m, 2250m, and 2600m. There is a slight altitude effect observed in the first sampling period, with lower atmospheric levels at higher altitude. However, in the other samplings this effect is not present. Although analytical errors and errors in the values of physico-chemical properties may have influenced the obtained results, comparison of the atmospheric levels by SPMDs and levels obtained by HiVols shows that both techniques give similar results. Like *Pinus uncinata*, the SPMDs can be used as passive air samplers on a broader spatial and temporal scale. Both techniques are cheap and fast to deploy on remote sites, like high-mountain areas. In this sense they could be used as monitoring systems to study the evolution of atmospheric OC levels in this sites. For the calibration of the uptake kinetics of SPMDs, PCB#155 can be used for exposure times of a few months. Exposure times of more than 3 months is recommended to obtain detectable OC levels.

7.2.1.3 Fate of OC in soils and lake sediment

The low concentrations of OC observed in the soils and sediments from the high-mountain lake areas indicate the absence of local pollution sources in their vicinity. The concentrations are in the same range as rural areas elsewhere and lower than in industrial areas, or rural areas in the UK. However, sediment concentrations are higher than soil concentrations. Studies of fallout of radionuclides have shown that the flux of Pb^{210} is slightly higher in soils than sediments, which indicates that the higher OC levels in sediments can not be explained by a soil erosion effect of particles from the catchment to the lake. Leaching of OC from the soils to the

lakes is also not probable since soil have relatively higher organic matter content than the sediments and OC have high K_{OW}. This points to retention of organochlorine compounds to the soils. In general, the soils and sediments have the same OC input (atmospheric deposition and gas exchange), so higher concentrations of OC in sediments could be explained by a higher retention efficiency of the sediments over the soils. The lake water column impedes re-volatilisation of OC once they have entered the lake, and no significant transformation processes occur in the water column (Vilanova et al., 2001a). In contrast, re-volatilisation in soil could take place. The temperatures of the bottom-water in the lakes is around 4ºC during whole the year, while soils can have values higher than 10ºC in warm periods (Catalan, 1992). These higher temperatures may enhance biological activities as well as re-volatilisation to the atmosphere after condensation or deposition.

The relative distribution of OC compounds in the vertical profile of soils and sediments points to a recent input of these compounds to the compartments (last 50 years). However, soils exhibit a wider spread in their profiles than sediments. In the later, OC are concentrated in a thin layer. The wider spread of OC in soils than sediments suggests biological activities, such as bioturbation, in the soils. The upper sections of the soils and sediments are dominated by the less volatile, or heavier molecular weight compounds. The predominance of these compounds could be a consequence of their predominant condensation at ambient temperature (Grimalt et al., 2001), since an important part of these compounds is in the atmospheric gas phase. However, another part of these compounds is in the particulate phase of the atmosphere, and may enter the lake area by deposition. The relative abundance of more volatile, or lighter molecular weight compounds in the deeper soil sections, and in some cases deeper sediment sections, can not be explained by differences in input mechanisms through time. It might be associated to vertical transport of these compounds in the soil and sediment column, caused by chemical diffusion, or rainfall dissolution and water table oscillations (Rapaport and Eisenreich, 1988). In addition, *in situ* formation of less chlorinated PCBs could also be one of the possibilities of the presence of these compounds in the deeper soil sections, after dechlorination of higher chlorinated PCBs under anaerobic conditions.

Radiometric analyses observe that all sediment cores have a rather uniform sedimentation within the lakes, but different sedimentation rates between lakes. The sediment cores are good stores of the historical pollution records, since no mixing has been observed. The sedimentation rates are not the same in all lakes, so the profiles of OC have different time resolutions. Ladove pleso shows a biannual resolution profile of PCBs increasing rapidly between 1949 and 1957. Before this time the levels were below limit of detection. Then, there is another increase between 1963 and 1970, a period that probably reflects the historical use of PCBs in Europe after WWII. HCB shows a similar trend. DDTs have a steep increase between 1955 and 1978. Then there is a strong drop between 1978 and 1990. The second increase between 1992 and 1997 could indicate a new period of DDT use in some parts of Europe or re-mobilisation of compound stored in environmental compartments. After 1997 the OC concentrations drop significantly. The sediment

cores from the other lakes, Estany Redon, Starolesnianske pleso and Dlugi staw, do not show this clear decrease. However, these sediment cores, which have their highest OC concentration in the top layer section, represent sedimentation inputs until 1994. Thus, before the drop in Ladove pleso took place. The vertical profile of OC concentrations in the sediments reflects the increase of OC production and use in Europe after WWII. Sediments from Ladove pleso may represent a drop in concentrations after 1997. This result suggests that the input of OC to the remote high-mountain lakes may be decreasing, at least in this part of Europe. The decrease of OC levels in sediments of industrial areas of the UK was related to the decrease of emissions after the prohibition of production and use of these products (Sanders et al., 1994).

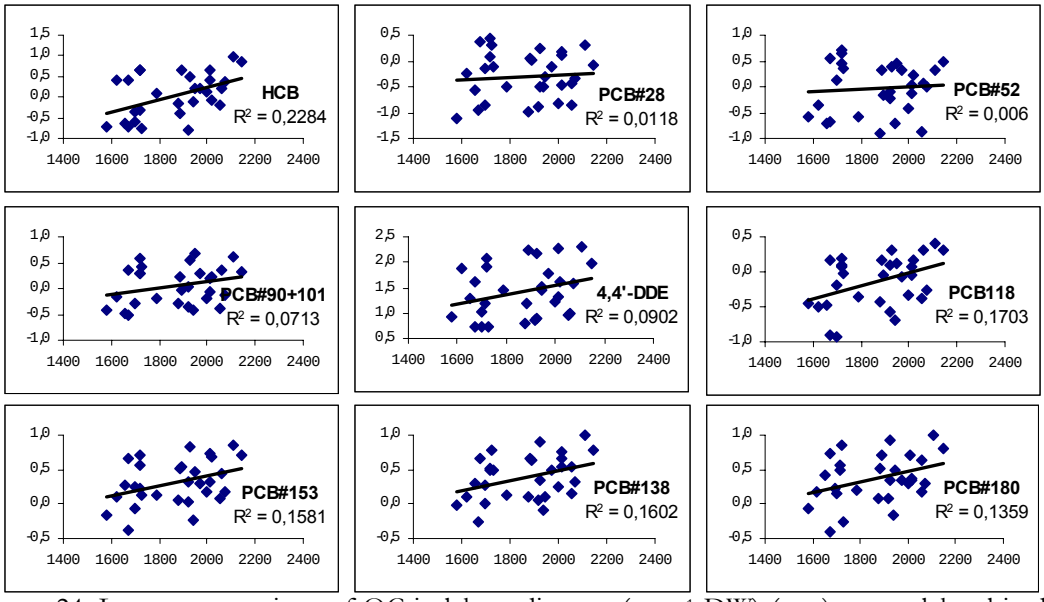

Figure 24. Log concentrations of OC in lake sediments (ng g^{-1} DW) (y-as) versus lake altitude (m) (x-as) of 30 high-mountain lakes in the High Tatras

A survey of 30 high-mountain lake sediments from the High Tatras sampled in 2001 shows a wide spread of OC concentrations in the top layer section (0-0.5cm) over this mountain range (Table 8; Figure 24). Ladove pleso (2057m) (**fat**) represents more or less the average OC concentrations in the lakes, with ΣPCB concentrations above the average and *4,4'*-DDE concentrations under the average. Lake Vyšné Terianske (2109m) shows highest OC concentrations while Zielony Staw Gąsienicowy (1672m) is the lake with the lowest ΣPCB concentrations and one of the lowest *4,4'*-DDE levels. These observations suggest that a selective trapping, or cold condensation effect takes place in this mountain range, since higher OC concentrations are found at higher (colder) altitudes than at lower altitudes. Moreover, the plots of the log concentrations of OC versus altitude of the lakes show positive slopes for most of the compounds (Figure 24). However, the altitude dependence of OC concentration in the lake sediments is not as clear as was observed in the comparison of lake sediments and fish muscle from lakes of different regions in Europe (Grimalt et al., 2001; Vives et al., 2004).

Table 8. OC concentrations (ng g-1 DW) in top layer (0-0.5cm) of high-mountain lake sediments of High Tatras (2001).

	Latitude °N	Longitude °E	Altitude (m)	ng/g DW									
				HCB	#28	#52	#90+101	4,4'-DDE	#118	#153	#138	#180	Σ PCB
Horné Roháčske	49,206	19,627	1718	4,5	1,2	2,9	1,9	80,8	1,2	3,7	3,2	3,7	17,8
Nižné Jamnícke	49,203	19,772	1728	0,2	0,8	2,3	2,7	5,2	0,9	1,4	3,1	0,6	11,8
Vyšné Račkove	49,200	19,807	1697	0,3	0,7	1,3	0,5	10,6	0,7	1,7	1,8	1,7	8,5
Zielony Staw Gąsienicowy	49,229	20,001	1672	0,2	0,1	0,2	0,3	5,4	0,1	0,4	0,5	0,4	2,1
Zelené krivánske	49,159	20,009	2017	0,8	1,3	1,7	1,7	42,2	1,5	4,8	4,5	2,3	17,8
Nižné Terianske	49,170	20,014	1941	0,8	0,3	0,2	0,4	28,7	0,2	0,6	0,8	0,7	3,2
Zadni Staw Polski	49,213	20,014	1890	4,6	1,0	0,7	0,9	168,3	0,9	3,6	4,4	5,1	16,5
Czarny Staw Gąsienicowy	49,231	20,020	1620	2,5	0,6	0,4	0,7	76,7	0,3	1,2	1,3	1,5	6,0
Vyšné Terianske	49,168	20,022	2109	9,3	2,0	2,0	4,2	200,6	2,5	7,3	9,7	10,1	37,9
Zmarzly Staw Gąsienicowy	49,224	20,024	1787	1,3	0,3	0,3	0,6	28,9	0,4	1,4	1,4	1,6	6,0
Vyšné Wahlenbergovo	49,164	20,027	2145	6,9	0,8	3,1	2,1	97,8	2,1	5,0	6,0	6,4	25,6
Czarny Staw Polski	49,205	20,028	1722	4,4	2,0	4,4	3,7	116,8	1,5	5,2	6,2	7,3	30,3
Nižné Temnosmrečinské	49,193	20,031	1674	2,5	2,3	3,7	2,2	41,2	1,5	4,6	4,5	5,3	24,1
Capie	49,168	20,038	2072	2,3	0,5	1,0	0,8	38,8	0,5	1,5	2,1	2,0	8,3
Vyšné Temnosmrečinské	49,189	20,040	1716	0,5	2,7	5,0	2,0	16,0	1,2	1,7	3,1	3,1	18,8
Wielki Staw Polski	49,213	20,040	1655	0,2	0,3	0,2	0,3	19,1	0,3	1,9	2,0	2,6	7,7
Malé Hincovo	49,174	20,059	1923	LQ	0,3	0,8	1,0	7,9	1,2	2,1	2,2	2,2	9,9
Veľké Hincovo	49,180	20,061	1946	1,6	0,5	2,8	4,7	33,1	1,3	2,9	1,3	3,2	16,6
Czarny Staw pod Rysami	49,189	20,078	1580	0,2	0,1	0,3	0,4	8,7	0,3	0,7	1,0	0,9	3,6
Veľké Žabie	49,172	20,079	1919	0,2	0,1	0,6	0,4	7,5	0,3	1,1	1,1	1,2	4,8
Dračie	49,166	20,088	1998	1,3	0,2	0,4	0,6	16,3	0,5	1,5	1,8	1,9	6,9
Vyšné Žabie bielovodské	49,194	20,094	1699	0,4	0,1	LQ	LQ	5,3	0,1	0,9	1,0	1,4	3,6
Ľadové pleso v Zlomiskách	49,163	20,108	1925	3,2	1,7	2,5	3,6	147,4	2,0	6,9	8,1	8,4	33,2
Batizovské	49,152	20,132	1879	0,7	0,1	0,1	0,5	6,1	0,4	1,1	1,3	1,2	4,7
Pusté	49,182	20,155	2055	0,6	0,1	0,1	0,4	8,9	0,4	1,2	1,4	1,5	5,2
Vyšné zbojnícke	49,179	20,160	1972	1,6	0,8	2,2	2,0	60,5	0,9	2,0	3,0	2,2	13,0
Ľadové pleso	**49,184**	**20,163**	**2057**	**1,7**	**0,4**	**1,2**	**2,2**	**9,9**	**2,1**	**2,7**	**3,5**	**4,2**	**16,3**
Žabie javorové	49,191	20,170	1886	0,4	1,1	2,1	1,7	15,3	1,5	3,4	4,6	3,4	17,7
Prostredné sivé	49,184	20,177	2011	4,7	1,5	1,0	1,6	179,8	1,2	5,5	5,9	5,2	21,9
Veľké spišské	49,193	20,196	2014	2,5	0,3	0,7	0,9	20,8	0,9	2,1	3,4	2,2	10,5

The absence of a significant altitude / temperature dependence in the High Tatras can be caused by different factors. In the case of the High Tatras the top layers of the sediments were sampled in 2001. All studied lakes have different sedimentation rates. Since no radiometric measurements were done on the top layers of the lake sediments it is not known if all top layers represent the period between 1997 and 2001. Probably they they do not. Thus, lakes with high sedimentation rates will be more diluted for OC levels than lake with low sedimentation rates.

7.2.2 Fate of polycyclic aromatic hydrocarbon in soils and sediments

Polycyclic aromatic hydrocarbons are emitted to the atmosphere constantly during combustion processes. Although they have relatively short atmospheric residence times they have been observed in considerable quantities in the high mountain atmosphere.

Table 9. Summary of average PAH concentrations observed at Skalnaté Pleso (High Tatras) (left) and Estany Redon (right).

	Gas (pg/m3)	Particulate (pg/m3)		Gas (pg/m3)	Particulate (pg/m3)
TSP (μg/m³)		16,9			14,3
Fluorene	915	29,1		88	1,4
Phenanthrene	3067	52,7		124	8,5
Anthracene	21	18,2		5	0,9
Fluoranthene	310	101,2		31	8,9
Pyrene	100	77,3		19	6,8
Benzo(a)anthracene	8	31,3		2	2,6
Chrysene+Triphenylene	20	63,9		4	8,6
Benzo(bj)fluoranthene	dl	68,3		dl	7,6
Benzo(k)fluoranthene	dl	41,5		dl	4,1
Benzo(e)pyrene	dl	46,2		dl	7,5
Benzo(a)pyrene	dl	41,4		dl	4,9
Indene(1,2,3cd)pyrene	dl	62,3		dl	6,7
Benzo(ghi)perylene	dl	55,3		dl	7,4
Dibenzo(ah)anthracene	dl	19,2		dl	2,9
ΣPAH	4442,8	707,8		290,1	85,1
June 2001	1971	420	November 2000	289,3	31,8
September 2001	3961	451	May. 2001	409,6	123,8
December 2001	11950	4571	February 2002	229,5	100,8
June 2002	4774	323	March 2002	232,3	454,1
			June. 2002	402,2	71,7
			January 2003	152,1	105,3

Table 9 shows the geometric means of PAHs at Skalnaté Pleso (High Tatras) and Estany Redon. The gas phase levels of the High Tatras are about 15 times higher than the levles in the Central Pyrenees. Particulate phase levles are about 8 times higher. The PAH levles of the High Tatras are also about 3 times higher than those of the Tyrolean Alps and the Norwegian mountains (Fernández et al., 2002). In the High Tatras the highest atmospheric PAH concentrations were

observed in the colder periods, which is consistent with the observations by Fernández et al. (2002). The PAH are about 4 times higher in winter than in summer. The increase of PAH in colder periods can be explained by the increase of PAH emissions from source areas, less dispersion due to stable atmospheric situations and a reduced photo-degradation in winter time. In the Central Pyrenees this seasonal differences are not that clear.

The upper sections of the soil and sediment cores from the High Tatras and Central Pyrenees are always dominated by the pyrolytic parent PAH, with a higher abundance of the heavier weight compounds of catacondensed structures. The levels are higher in the High Tatras than in the Central Pyrenees, which is consistent with observed atmospheric levels. But despite the variability in sources and total PAH load, the distributions of the PAH in the sediments are very similar. The uniform sedimentary PAH profile exhibits a high parallelism with the PAH composition of the aerosols at these sites (Fernández et al., 2002). This composition is source independent and PAH load, and is very typical of air masses at remote locations.

Comparison between sediments and soils shows that the PAH ratios observed in the later are closer to the ones observed in aerosols. The transport through the water column to the sediments may be responsible for transformation of the PAH composition. However, the down core PAH ratios are less variable in the sediments than in the soils. Once the PAH have been buried the PAH are better preserved in the sediments than in the soils.

Radiometric dating of the sediment cores give different sedimentation rates for the lakes and thus different time resolutions of the vertical PAH profile in the cores (see 7.2.1.3). Ladove Pleso shows a biannual record between from 1924 and 2001, while the other lakes have lower temporal resolutions. The sediments from Ladove Pleso shows that the PAH levels between 1924 and 1954 were much lower than after 1954. In the other lakes the PAH levels maintain rather constant values from 1821 (earliest sample year) to the beginning of the 20th century. The steep increase of sedimentary PAH in the first half of the 20th century is observed in all lakes and can be interpreted as the effect of the increasing combustion of fossil fuels in this period, in coincidence with the industrial revolution and further intensification of the industry. Especially in the Tatras, high PAH levels are observed, which reaching concentrations 10 times higher than before the increase. There is a maximum in the Ladove Pleso core between 1980 and 1988 and between 1963 and 1966. The strong decrease of PAH levels from 1988 to 2001 (latest sample year) is consistent with the improvement of combustion techniques in central Europe and thus may indicate a decrease of atmospheric PAH emissions. The absence of the PAH decrease in the other lakes may be caused by the fact that their temporal resolution is lower than Ladove Pleso and their latest sample year is 1994, instead of 2001.

All pyrolytic PAH show a very similar temporal trend, reflecting similar atmospheric input through time to European mountain areas. However, perylene and retene exhibit a different profile with time in Estany Redon for the former and in all lake for the later. Perylene shows its highest concentrations in the oldest sediment sample in Estany Redon, while retene levels do not differ too

much between new and old sediments. The increase of perylene in the Redon sediments with depth is probably caused by in situ production of this compound. Although its precursor is still unknown, it is likely to be related to higher plant residues. The lack of anoxic conditions in the soil may be responsible for the absence of a perylene increase with depth in the soils. Retene has been used as a marker for wood combustion, while benzo(b)naphto[2,1-d]thiophene (BNT) is a specific marker for coal combustion. The relative constant retene concentrations in the sediment cores of the lakes may indicate a constant input of this compound after wood combustion. The increase of pirolytic PAH after combustion of fossil fuels may be represented by BNT. So, the ratio between these two ´markers´ may indicate the downcore variation between ´natural´ and ´industrial´ combustion. A similar index is proposed for 1,7-dimethylphenenthrenes vs 2,6-dimethylphenenanthrene, the first being a marker for wood combustion and the later a marker for fossil fuel combustion. The retene/(retene+BNT)-index increase with depth in Redon soils and in sediments and sediments from Ladove Pleso, while the 1,7DMPhe/(1,7DMPhe+2,6DMPhe)-index is constant with depth in soils and sediments. The downcore increase of the retene/(retene+BNT)-index indicates a diagenetic production of retene in the sediments. Thus, in these mountain environments this compound can not be used as marker for wood combustion.

7.3 Global atmospheric fate of POP with PCBs as model compounds

The atmospheric residence times of PCBs with the Junge model are higher than the residence times estimated by using the OH radical reactions of Anderson and Hites (1996b). Application of the reaction rates, as observed by Anderson and Hites (1996b), on environmental data would result in orders of magnitude faster depletion of the less chlorinated PCBs (more reactive) in comparison with the more chlorinated PCBs (less reactive). If this fast depletion of less chlorinated PCB really takes place in the troposphere, then this should be observed in the samples from environmental compartments. However, there are no temporal and spatial trends that give evidence for such enhanced depletion of less chlorinated PCBs. For example, the composition of PCB congeners is more or less the same along historical samples, such as sediment cores (Sanders et al., 1995; article 7). Moreover, the estimated quantity of degraded PCBs is of such an order that it outnumbers the loss of PCBs from the environment by other processes, such as sink to oceanic sediments. But maybe more important is the fact that PCBs are still detected in remote atmospheres (article 1, 4). This means that a constant flux of PCBs from sources to the atmosphere is required to maintain these actual ambient PCB concentrations. Even in a scenario of maximum annual PCB emissions (Breivik et al., 2002) this would not be enough by orders of magnitude to compensate for the annual loss of PCBs by the presumed OH radical reactions. On the other hand, even if atmospheric PCB levels are decreasing, it seems that this decrease is similar for the different PCB congeners (article 7).

As mentioned before, the experimental conditions under which the PCB-OH reaction rate constants were obtained are to far from the environmental conditions. Application of these rate constants may therefore lead to overestimation of the atmospheric loss of PCBs, especially the more volatile and reactive congeners.

Calculations of the τ_{total} with the Junge model indicates that less chlorinated PCBs (3CB, 4CB and 5CB) have similar or slightly lower residence times than the more chlorinated PCB (6CB and 7CB, and probably 8CB) (article 11, Fig. 5). These results might indicate that the OH reactions have influence on the less chlorinated PCBs, but that the reaction rates are not the ones calculated by Anderson and Hites (1996b). Application of the Junge model to estimate the tropospheric residence time of PCBs does not allow to elucidate which fraction is removed irreversibly from the troposphere (photo-degradation) and which fraction is removed reversibly (deposition). Deposited PCB could re-volatilise and return to the tropospheric PCB pool. However, there is no evidence based on field measurements that such depletion takes place. One way or another, the findings show that there is still a wide gap of knowledge in the understanding of the atmospheric fate of these compounds. Among other requirements, more measurements in the tropical zone on both hemispheres are needed to obtain better estimates on global atmospheric levels, and consequently, better approaches on PCB losses.

Chapter 8 Conclusions

Chapter 8. Conclusions

1) In the free-troposphere of the tropospherical Atlantic, the atmospheric organochlorine compounds and polycyclic aromatic hydrocarbons are well mixed and predominantly present in the gas phase. Back-trajectories show little influence from potential regional source areas, such as the European continent. The atmospheric OC levels and composition of the air masses origin from long-range atmospheric transport in the subtropical part of the free-troposphere.

2) In the European high-mountain atmosphere, HCB, PCBs, 4,4´-DDE are also relatively well mixed. HCB and the more volatile PCB-congeners are pre-dominantly present in the gas phase. The transport of these OC to these high-mountain areas is related to LRAT, but the origin of the compounds is mainly related to surface sources located in Europe.

3) In the European high-mountain atmosphere, the atmospheric variability of HCHs and endosulphanes is related to the application of these products for agricultural purposes in the European continent.

4) Some evidence is found for the degradation of PCBs by OH-radicals. The vertical gradient is decreasing with increasing chlorine number.

5) In the free-troposphere, there is a relatively constant settling flux of organochlorine compounds in the dry deposition mode. Variability in atmospheric deposition is essentially caused by episodes of wet deposition, which increases the settling flux of the more volatile and water soluble compounds.

6) In the free-troposphere (above the inversion layer of the subtropical Atlantic), where the soils are relatively poor in organic matter, adsorption of atmospheric PAH to soil soot-carbon is the dominant sorption process. Below the inversion layer the sorption of PAH to soils is controlled by their high organic matter content.

7) Leaves from *Pinus uncinata* are useful as passive atmospheric samplers for organochlorine compounds. The pine needle-air partitioning coefficients increase with decreasing temperatures, which explains the higher PCB concentrations in *Pinus uncinata* at higher altitude (lowest ambient tempeautre). A selective trapping / cold condensation effect is observed on these leaves.

8) SPMDs are useful as passive atmospheric samplers for organochlorine compounds. However, there are uncertainties related to the model calculation in order to obtain environmental OC levels.

In any case, the atmospheric OC concentrations obtained by SPMDs are in good agreement with the results obtained by HiVol pumping.

9) In the European high-mountain soils and lake sediments, organochlorine compounds are better preserved in the sediments than in the soils. All samples show an increase of OC after 1940, with higher absolute levels in the High Tatras than in the Central Pyrenees. The sediment core from Ladove Pleso shows a decrease of all OC in the last decade, indicating a decrease of atmospheric OC input to the High Tatras.

10) Higher PAH levels are observed in the soils and sediments of the High Tatras, than in the Central Pyrenees. The surface soils reflect better this difference than the sediments. Transport through the water column to the sediments may be responsible for the transformation of the PAH composition. However, once the PAH have been buried, PAH are better conserved in the sediments. The increase of PAH levels is related to the Industrial Revolution and the intensification of industrial processes in the European continent. The sediment core from Ladove Pleso shows a PAH decrease in the last decade, indicating a decrease of atmospheric input load to the High Tatras.

11) The Global atmospheric PCB pool shows 2-3 times higher amounts of PCBs in the Northern Hemisphere than in the Southern Hemisphere, which is in agreement with the historical production and use of these compounds. Modelisation of sink processes by OH radical degradation or estimated tropospheric residence times, gives rise to large annual sink differences between the two approaches. Extrapolation of laboratory derived reaction rates to tropospheric PCB levels yields large discrepancies between the annual atmospheric PCB sink and the annual emission and sinks in other environmental compartments.

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